Canadian Journal of Fisheries and Aquatic Sciences (Supplement)

Journal canadien des sciences halieutiques et aquatiques (Supplément)

Volume 40, Supplement No. 2, 1983

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Proceedings of the Conference on Pollution in the North Atlantic Ocean

Canada

Fisheries and Oceans Pêches et Océans

Canadian Journal of Fisheries and Aquatic Sciences (Supplement)

Journal canadien des sciences halieutiques et aquatiques (Supplément)

Government of Canada
Fisheries and Oceans

Scientific Information and Publications Branch
Ottawa K1A 0E6

Gouvernement du Canada
Pêches et Océans

Direction de l'information et des publications scientifiques
Ottawa K1A 0E6

Volume 40, Supplement No. 2, 1983

Volume 40, Supplément n° 2, 1983

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Canadian Journal of Fisheries and Aquatic Sciences (Supplement)

Journal canadien des sciences halieutiques et aquatiques (Supplément)

Volume 40, Supplement No. 2, 1983

Volume 40, Supplément n° 2, 1983

Correct citation for this publication:
FARRINGTON, J. W., J. H. VANDERMEULEN, AND D. G. COOK [ed.] 1983. Proceedings of the Conference on Pollution in the North Atlantic Ocean. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 1–362.

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Editor's Foreword

The ubiquitous and serious nature of man's impact on the biosphere is perhaps illustrated most dramatically by the inescapable fact that our activities are contaminating[1] at least parts of our oceans. The Journal is pleased to publish selected papers from a unique and challenging conference that focussed on this subject of international concern: Ocean Pollution 1981, convened in Halifax, Nova Scotia, October 19–23, 1981. The Conference was conceived and chaired by Drs J. H. Vandermeulen (Bedford Institute of Oceanography) and J. W. Farrington (Woods Hole Oceanographic Institution — WHOI) and cosponsored by their institutions, which comprise two major east coast centers of oceanographic research. Financial support for the meeting and publication of the proceedings was provided by the Office of Marine Pollution Assessment, National Oceanic and Atmospheric Administration, U.S. Department of Commerce; a grant from the Andrew W. Mellon Foundation to the Coastal Research Center, WHOI; and Ocean Science and Surveys, Canadian Department of Fisheries and Oceans.

For 4½ d, some 80 working scientists from North America and Europe and 40 observers (including some from the Caribbean, South Africa, and East Germany) reported and discussed progress towards establishing the nature and extent of pollution in the North Atlantic and the processes that control the distribution of contaminants. The facts are that a number of coastal areas are polluted (according to any definition) and that contaminants continue to enter the sea, probably at increasing rates. With the improved accuracy and precision of modern analytical techniques and the power of electronic data processing, it is becoming scientifically and economically feasible to monitor the status of the ocean and to advance significantly our understanding of its physical and chemical processes. I believe that these Proceedings challenge politicians, regulatory agencies, and research managers worldwide to finance and to nurture this long-term research so that the "desired uses [of our oceans] are not unwittingly abrogated" (Farrington and Vandermeulen, this issue).

D. G. Cook
Assistant Editor

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[1]The terms "pollution" and "contamination" are used interchangeably in many papers in this volume. As Professor Michael Champ points out in his introductory note, definitions vary with the time and context of usage.

Printed in Canada (J7349)
Imprimé au Canada (J7349)

Avant-propos du rédacteur

Le fait inévitable que nos activités contaminent[1] au moins certaines parties de nos océans met dramatiquement en lumière le caractère sérieux et omniprésent de l'influence de l'homme sur la biosphère. La conférence « Ocean Pollution 1981 », tenue à Halifax (Nouvelle-Écosse) du 19 au 23 octobre 1981, s'est concentrée sur ce sujet d'intérêt international et le *Journal* a le plaisir d'en publier certaines communications. La conférence, d'un caractère unique et provocateur, a été conçue et présidée par les Drs J. H. Vandermeulen (Institut océanographique de Bedford) et J. W. Farrington (Woods Hole Oceanographic Institution — WHOI) et parrainée conjointement par leurs établissements, qui constituent deux principaux centres de recherche océanographique sur la côte est. L'appui financier pour la réunion et la publication du compte rendu a été fourni par les organismes suivants : Office of Marine Pollution Assessment, National Oceanic and Atmospheric Administration, U.S. Department of Commerce; une subvention de l'Andrew W. Mellon Foundation to the Coastal Research Center, WHOI; et Sciences et Levés océaniques, du ministère des Pêches et des Océans du Canada.

Pendant 4½ jours, quelque 80 scientifiques nord-américains et européens et 40 observateurs (dont certains des Caraïbes, de l'Afrique du Sud et de l'Allemagne de l'Est) ont présenté des rapports et discuté des progrès dans la détermination de la nature et de l'étendue de la pollution dans l'Atlantique nord et des processus qui contrôlent la dissémination des éléments polluants. Il est établi qu'un certain nombre de zones côtières sont indéniablement polluées et que des éléments polluants continuent à s'infiltrer dans les mers, probablement à des taux croissants. La précision et l'exactitude croissantes des méthodes analytiques modernes et la puissance de l'informatique rendent économiquement et scientifiquement possibles la surveillance de l'état de l'océan et l'approfondissement de notre compréhension des processus physiques et chimiques. Je suis d'avis que ce compte rendu encouragera les hommes politiques, les organismes de réglementation et les gestionnaires de la recherche du monde entier à financer et à entretenir cette recherche à long terme afin que « l'usage désiré ne soit pas inconsciemment supprimé » (Farrington et Vandermuelen dans le présent volume).

D. G. Cook
Rédacteur adjoint

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[1]Les termes « pollution » et « contamination » sont utilisés l'un pour l'autre dans de nombreux articles de ce volume. Comme le fait remarquer le professeur Michael Champ dans son allocution de bienvenue, les définitions varient selon le temps et le contexte.

Etymology and Use of the Term "Pollution"

MICHAEL A. CHAMP

The American University, Washington, DC 20016, USA

Through the decades of the 1950's, 1960's, and 1970's the popular media used the term "pollution" widely as a generality (such as "Lake Erie is polluted"), usually with no reference to the degree or state of pollution. Many scientists were asked to determine "how polluted" or "by what" with reference to preventative or corrective measures. Probably every major river, stream, and lake, and most of the coastal zone in the lower 48 states has been sampled to determine if it is polluted and, if so, how polluted.

But what is pollution? Is it a social or scientific concept? Many times I have slipped the question "define pollution" into a student's comprehensive exam, hoping to learn the answer. I found out early that most quantified their answer only in environmental terms, such as increased level of contaminant(s), oxygen depletion, increased chlorophylls, decreased taxa, or increased abundance of contaminant-tolerant organisms.

A National Academy of Sciences Workshop on the Tropospheric Transport of Pollutants to the Ocean concluded the following (U.S. NAS 1978):

> The term pollutant is not definitive. An element or compound injected into the environment as a consequence of Man's activities is not a pollutant *per se*; it becomes a pollutant when its distribution, concentration, and chemical or physical behavior are such as to have undesirable or deleterious consequences. Thus, attaching a label of pollutant to a specific material presumes a considerable knowledge about its impact on the environment; knowledge that, for the most part, is lacking for the marine environment.

Only a few authors have contributed scholarly deliberations regarding the use and definition of the term pollution (Warren 1971; Mackenthun 1973; U.S. NAS 1978; GESAMP 1980; Geyer 1981). A review of the origin and previous usage of this word is required to understand its present usage. The best historical review is found in Warren (1971), who reports that the word pollution is an adaptation of the Latin "pollutionem," meaning defilement, and from "pollutus," past participle of "polluere" — to pollute, to soil or defile, or to desecrate (Webster's Third International Dictionary 1971). It was used in its present form, "pollution," in France in the twelfth century. The Oxford English Dictionary documents its Middle English usage dating from the fourteenth century. Its early English usage was associated with "defilement of man, his beliefs, or his symbols by physical, moral, or spiritual contamination or uncleanness." Webster's New Collegiate Dictionary (1979) gives the Middle English preferred definition of pollution as "emission of semen at other times than in coitus."

In the 1950's many investigators began to study the effects of contaminants in streams, rivers, and lakes. During and following this period, many definitions of pollution arose, primarily in relation to the environment:

Coulson and Forbes (1952):

> The addition of something to water which changes its natural qualities so that the riparian proprietor does not get the natural water of the stream transmitted to him.

McKee (1952):

> Means an impairment, with attendant injury, to the use of the water that plaintiffs are entitled to make. Unless the introduction of extraneous matter so unfavorably affects such use, the condition created is short of pollution. In reality, the thing forbidden is the injury. The quantity introduced is immaterial.

Patrick (1953):

> Anything which brings about a reduction in the diversity of aquatic life and eventually destroys the balance of life in a stream.

Printed in Canada (J7364)
Imprimé au Canada (J7364)

Ide (1954):

> Any influence on the stream brought about by the introduction of materials to it which adversely affects the organisms living in the stream.

U.S. Public Health Service (1962): For the purpose of Drinking Water Standards means "the presence of any foreign substance (organic, inorganic, radiological, or biological) in water which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water."

U.S. President's Science Advisory Committee (1965):

> The unfavorable alteration of our surroundings wholly or largely as a by-product of man's actions, through direct or indirect effects of changes in energy patterns, radiation levels, chemical and physical constitution, and abundances of organisms. These changes may affect man directly, or through his supplies of water and of agricultural and other biological products, his physical objects or possessions or his opportunities for recreation and appreciation of nature.

National Research Council Committee on Pollution (U.S. NAS 1966):

> An undesirable change in the physical, chemical, or biological characteristics of our air, land, and water that may or will harmfully affect human life or that of other desirable species, our industrial processes, living conditions, and cultural assets; or that may or will waste or deteriorate our raw material resources.

Warren (1971):

> An impairment of the suitability of water for any of its beneficial uses, actual or potential, by man-caused changes in the quality of the water.

U.S. Congress (1978): The term ocean pollution "means any short-term or long-term change in the marine environment."

GESAMP (1980):

> The introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities.

This is also the Intergovernmental Oceanographic Commissions' (IOC) definition.

Geyer (1981): Makes numerous comparisons of "natural" and "man-made" pollution (i.e. "the Amazon each day dumps 3×10^6 tons of fine sediments into the Atlantic") and suggests that "all too often reactions to pollution on the part of many have been one of subjectivity rather than objectivity; and emotionalism overcoming logic to severely cloud reasonable perspectives in evaluating a given pollution situation."

Champ (1975):

> Any man-made alteration of the existing environment that adversely affects the natural quality and quantity of the environment for life. I also have observed that most natural ("Mother Nature") pollution events are of short duration or non-continuous (i.e., flood — maximum 7–10 days' disturbance), whereas man-made is usually of much longer duration (months, years, etc.). Exceptions to this would be: (1) natural oxygen depletion and associated benthic mortalities in the New York Bight in 1976; (2) "Red tide" algal blooms with massive toxicity-related mortality; (3) naturally occurring oil seeps; and (4) eruptions (Mount St. Helens [1982], etc.). These events, due to their non-continuity, appear to be survival of the fittest testing grids, exerting evolutionary pressures to selectively expand the tolerance of species or to eliminate non-successful genes from the breeding stock.

On November 4, 1977, the U.S. Congress amended the Marine Protection, Research, and Sanctuaries Act (Public Law 92-532, commonly referred to as the Ocean Dumping Act, see U.S. Congress 1972) so that ocean dumping of "harmful" sewage sludge would not be allowed after December 31, 1981. This Federal law defines "harmful" sewage sludge to be "any solid, semisolid, or liquid waste generated by a municipal wastewater treatment plant, the ocean dumping of which may unreasonably degrade or endanger human health, welfare, amenities or the marine environment, ecological systems or economic potentialities" (33 USC 1411, 1412a). The U.S. Environmental Protection Agency (U.S. EPA) interpreted this requirement to prohibit all ocean dumping of sewage sludge, because sewage sludge failed U.S. EPA's ocean dumping criteria (bioassay tests). The U.S. EPA's interpretation was challenged by the City of New York in Federal Court (The City of New York vs the U.S. EPA). The City contended that land-based alternatives

are less socially and economically desirable than ocean dumping. The U.S. District Court (1981) ruled in favor of New York City, imposing a balancing requirement in which the U.S. EPA must weigh the financial costs and environmental impacts of land-based alternatives and the effects of dumping at the dumpsite in determining the unreasonableness. In essence, this action requires a Federal agency to assess social, economic, and environmental impact data to determine the acceptability of a polluting act. A polluting act is deemed acceptable if there is a lack of "unreasonable" degradation when compared with the social, economic, or environmental burden imposed by the alternatives.

The variety of usage is derived from the perspectives of (1) chemists: presence of contaminants, (2) biologists and ecologists: effect on organisms and on ecosystems, and (3) policy or decision makers: impairment of water use or benefit (resource value).

The future use of "pollution" will require an integration of these three perspectives or we will continue with our debate. David A. Flemer (U.S. EPA, Chesapeake Bay Research Program, Annapolis, MD 21401, personal communication) in reviewing this manuscript focused on this and defined pollution "as the introduction or redistribution of energy or materials through human activities that affects ecological processes which alters an ecosystem's output of goods and services from a defined reference state". We define "goods" as renewable resources, "services" (i.e. waste assimilation), and "state" as spatial and temporal boundaries with judgmental values of a system defined in part by use. This definition separates roles, it recognizes the responsibility that scientists have in making technical assessments of ecosystem processes (including structure and function) as influenced by human activities, and it leaves to the policy and decision maker (the publicly *elected* official) to assess and interpret social values. A clear distinction of roles is needed to prevent loss of objectivity and credibility. The environmental movement is suffering today from a swing of the pendulum that is in part brought about by this and economic conditions.

In summary, "pollution" has become another "dinner table" or "news media" term and should be viewed as a social and political concept and not a scientific one. Its environmental connotation is relative to social and political values and, in my opinion, economic conditions of a given period.

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Introduction to Ocean Pollution 1981

JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

AND JOHN W. FARRINGTON

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

There is a continuing and evergrowing need for scientific assessment and evaluation of real and potential pollution problems as increasing kinds and amounts of man-mobilized chemicals that are foreign to the undisturbed environment are being detected in the sediments, waters, and biota of the world's oceans. The Woods Hole Oceanographic Institution and Bedford Institute of Oceanography agreed to cosponsor an international scientific conference to focus on the status of our knowledge of ocean pollution as a contribution towards satisfying some of these needs.

In our earliest discussions, we were very much aware of the large — if not excessive — number of various types of conferences, symposia, and workshops dealing with ocean pollution problems. Indeed, we were cautioned by several colleagues that there were already too many of these meetings. We contended that the majority of these meetings focused on interfacing available scientific knowledge with policy or management issues. While recognizing the obligations of scientists to participate in these types of meetings, we sought instead to convene a conference where scientists would come together to discuss new research results and exchange the latest ideas and information. Tractable objectives for the conference were to establish the status of our knowledge and research needs for inputs and distributions of pollutants and processes controlling these distributions in the North Atlantic region. While these issues are of global concern, the North Atlantic region was a logical choice because (1) our assessment of the literature suggested that we know more about chemical pollution in the North Atlantic than any other ocean, (2) a variety of research and monitoring programs have been ongoing on the coast bordering the North Atlantic, particularly Canada, the United States, and Europe, (3) there is increasing pressure in various North Atlantic rim-countries to use and even expand the use of the North Atlantic as a receptor of chemical wastes, and (4) the geographical location of the sponsoring organizations and the research interests of many of their scientists made it logical to sponsor such a conference.

With these considerations as a background and rationale, about 100 marine scientists from around the North Atlantic met in Halifax in October 1981 to discuss, through invited and contributed papers, the state and processes of chemical contamination of that marine environment, incuding the waters of the Gulf of St. Lawrence, Davis Strait, Gulf Stream, North Sea, and Baltic Sea. The focus of the conference was limited to the physicochemical aspects of pollutants, exploring and hopefully delineating the various inputs, routes, and rates of movements of these pollutants through the North Atlantic ecosystems, and attempting to assess their short- and long-term fates. It is recognized, of course, that the biological and physical effects of chemical pollutants are of utmost importance. A discussion on the latter, however, would likely overwhelm any discussion of their physical distribution. In our view, then, an important approach toward understanding oceanic pollution and toward raising our awareness of this potential global problem begins with establishing levels of contaminants and describing the processes mediating their movements, fates, and bioavailability. Subsequently, we can, in future conferences, turn to their effects.

The second limitation we set was to exclude papers and discussions on radionuclides. We felt that this particular subject was of too large a scope to be included within the week's discussions and that we simply would not be able to give this subject its due recognition.

Printed in Canada (J7251)
Imprimé au Canada (J7251)

The conference, and these proceedings, consist of four sessions, following one after the other so that all participants were able to attend and participate in all presentations. While most papers focused on one or another aspect of chemical contaminant levels and distribution in oceanic waters, we also invited and included studies of a more experimental nature where these served to further illustrate some particular phenomenon or process. The agenda allowed for ample discussion and question time, and in fact we realized an atmosphere of collegiate and congenial thought and exchange with a lively interchange of ideas. Session cochairmen provided synopsis notes, which we combined with our own impressions of the papers and discussions to provide a summary and some general thoughts for future activities.

The session on ocean dumping was included in the conference because of the current special interest in this topic. This session is summarized separately because of its special nature.

In retrospect, we are satisfied with the outcome of this first conference on ocean pollution. The more serious aspects of ocean pollution are, for now, mainly local problems contained in coastal waters. Research of the type presented in the conference papers contributes knowledge necessary for defining, confirming, and abating these current problems. However, we cannot be satisfied with the limits of our present knowledge. The trend towards continued and increased use of the oceans for disposal of waste requires accelerated research and monitoring efforts. For these reasons, we sincerely hope that there will be future ocean pollution conferences in other parts of the world so that we can be reasonably certain to avoid serious human health problems and also to avoid widespread, long-lasting adverse impacts on the valuable natural resources of the oceans.

Acknowledgments

We thank all of the conference participants, especially the keynote speakers and session chairmen, for their valuable contributions which provided the essential ingredients for worthwhile scientific interactions. The conference could not have taken place without the indispensable assistance of the secretarial and administrative personnel of our institutions. A special note of gratitude is extended to Dr John M. Teal, who filled in for one of us (J.W.F.) during a period of illness. He added his extensive marine ecology experience, which broadened the perspectives of discussion.

SESSION I

Fossil Fuel Hydrocarbons

CO-CHAIRMEN

JAMES N. BUTLER

Department of the Environmental Sciences, Harvard University, Cambridge, MA 02138, USA

AND DONALD C. MALINS

Environmental Conservation Division, Northwest and Alaska Fisheries Center, National Marine Fisheries Service, NOAA, Seattle, WA 98112, USA

Input of Pelagic Tar into the Northwest Atlantic from the Gulf Loop Current: Chemical Characterization and its Relationship to Weathered IXTOC-I Oil[1]

E. S. VAN VLEET, W. M. SACKETT, F. F. WEBER JR.,[2] AND S. B. REINHARDT

Department of Marine Science, University of South Florida, 830 First Street South, St. Petersburg, FL 33701, USA

VAN VLEET, E. S., W. M. SACKETT, F. F. WEBER JR., AND S. B. REINHARDT. 1983. Input of pelagic tar into the Northwest Atlantic from the Gulf Loop Current: chemical characterization and its relationship to weathered IXTOC-I oil. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 12–22.

Pelagic tar concentrations have been measured for samples collected monthly in the eastern Gulf of Mexico over a one year period. Analyses of the pelagic tar included gravimetric, isotopic ($\delta^{13}C$) and molecular (gas chromatographic) characterization of the total, aliphatic, and aromatic fractions. The concentrations of pelagic tar ranged from 0 to 26.5 mg $\cdot m^{-2}$ of toluene extractable material, with an average of 1.60 mg$\cdot m^{-2}$ in the offshore neuston tows and 0.05 mg$\cdot m^{-2}$ in neuston tows taken on the west Florida continental shelf. Oblique tows to 100 m depth averaged 0.01 mg$\cdot m^{-2}$. $\delta^{13}C_{PDB}$ values for the total tar in each tow averaged −27.2‰ with the aliphatic fractions averaging −27.5‰ and the aromatic fractions averaging −27.0‰. Approximately 40% of the tar samples showed a bimodal *n*-alkane distribution characteristic of crude oil sludge. Based upon an average annual Loop Current discharge of 28×10^6 $m^3 \cdot s^{-1}$ through the Florida Straits, it is estimated that approximately 7000 t of pelagic tar are discharged annually from the Gulf of Mexico into the North Atlantic. Approximately half of this may be brought into the Gulf from the Caribbean via the Loop Current, while the remainder appears to originate in the Gulf of Mexico. Possible origins of the floating tar include input from the Caribbean Sea through the Yucatan Strait, production and transportation operations in the Gulf of Mexico, Mississippi River discharge, subsurface oil seeps, and major accidental discharges. Large amounts of oil from the IXTOC-I well blowout do not appear to have impinged on coastal waters of Florida.

VAN VLEET, E. S., W. M. SACKETT, F. F. WEBER JR., AND S. B. REINHARDT. 1983. Input of pelagic tar into the Northwest Atlantic from the Gulf Loop Current: chemical characterization and its relationship to weathered IXTOC-I oil. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 12–22.

Les concentrations de bitume pélagique ont été mesurées dans des échantillons recueillis mensuellement dans le secteur oriental du golfe du Mexique durant une année. Les analyses comprennent la détermination des propriétés gravimétriques, isotopiques ($\delta^{13}C$) et moléculaires (chromatographiques en phase gazeuse) des fractions totale, aliphatique et aromatique. Les concentrations de bitume pélagique sont comprises entre 0 et 26,5 mg$\cdot m^{-2}$ de matériel extractible au toluène, avec moyenne de 1,60 mg$\cdot m^{-2}$ dans les prises de neuston du large et de 0,05 mg$\cdot m^{-2}$ dans celles du plateau continental de la Floride occidentale. Dans les traits obliques à une profondeur allant jusqu'à 100 m, les valeurs moyennes sont de 0,01 mg$\cdot m^{-2}$. Les valeurs de $\delta^{13}C_{PDB}$ pour le bitume total recueilli dans chaque trait sont en moyenne de −27,2 ‰, les fractions aliphatiques étant de −27,5 ‰ et les fractions aromatiques −27,0 ‰. Environ 40 % des échantillons de bitume montrent une distribution bimodale de *n*-alcane, caractéristique des boues à pétrole brut. On estime, en se fondant sur le débit annuel moyen du courant de maille du golfe de 28×10^6 $m^3 \cdot s^{-1}$ à travers le détroit de Floride, qu'environ 1000 t de bitume pélagique sont déversées annuellement par le golfe du Mexique dans l'Atlantique nord. Environ la moitié de cette quantité a pu être introduite dans le golfe en provenance des Caraïbes via le courant de maille, tandis que la balance semble provenir du golfe du Mexique. Parmi les origines possibles de ce bitume, on note les apports de la mer des Caraïbes par le détroit de Yucatan, les opérations liées à la production et au transport dans

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: EXXON Production Research Co., P.O. Box 2189, Houston, TX 77001, USA.

Printed in Canada (J6841)
Imprimé au Canada (J6841)

le golfe du Mexique, le débit du Mississippi, les infiltrations de pétrole sous le surface et les déversements accidentels majeurs. Les grandes quantités de pétrole résultant de l'éruption du puits IXTOC-I ne semblent pas avoir envahi les eaux côtières de Floride.

Received March 18, 1982
Accepted September 27, 1982

Reçu le 18 mars 1982
Accepté le 27 septembre 1982

DURING the past 10–15 yr, the presence of heavy oil in the open ocean, henceforth referred to as pelagic tar, has attracted considerable attention. The concentration of floating tar varies widely in different parts of the world (Wong et al. 1976; Levy 1977; Jeffrey 1980). Based upon indirect evidence from the high wax composition and high iron-content of pelagic tar, as well as known tanker routes, Butler et al. (1973) and McGowan et al. (1974a, b) have suggested that the largest single source of floating oil residues is from the discharge of tanker washings and ballast by crude-oil tankers (NAS 1975). An increased global demand for oil in recent years has led to a concurrent increase in exploration, drilling, and shipping activities. The oil fields offshore Mexico are thought to approach those of the Middle East in size and will probably be producing 2.5 million barrels per day by the end of the 1980s. Offshore leasing, exploration, and oil well drilling have also recently begun off the west Florida coast and will continue over the next several years. Drilling, production, and marine transportation activities throughout the Gulf are expected to increase manyfold compared to today's activities. The frequency and magnitude of oil spillage will also probably increase proportionately. In addition, two disastrous oil spills occurred in the Gulf of Mexico in 1979 and contributed to the already high background levels of pelagic tar occurring in the Gulf. The IXTOC-I drilling blowout and the collision of the oil tanker, *Burmah Agate*, offshore Galveston, Texas, released more than 3 000 000 and 390 000 barrels of petroleum, respectively.

The major incident which precipitated concern over the threat of oil pollution in coastal waters of Florida was the IXTOC-I blowout on June 3, 1979 in the southwestern Gulf of Mexico in the Bay of Campeche (19°24′N, 92°19′W). Initially, it was estimated that 30 000 barrels (5×10^6 L) of crude oil were escaping daily from the well. Two months later (August 16, 1979), as the well continued to spill oil into the Bay of Campeche, oil from the blowout began to wash up on the beaches of the south Texas barrier islands, 800 km away. The well continued to release oil for a total of 9 mo until it was successfully capped on March 23, 1980. By that time approximately 5.1×10^8 L (134 million gal) of crude oil had been released by the IXTOC-I well (Geo-Marine 1980). The fate of that oil was and still is uncertain.

It was in the climate of these recorded and likely new disasters that the State of Florida undertook a program aimed at protecting its coastal environments by maintaining an attentive surveillance of the offshore waters of the west Florida continental shelf. This surveillance was to be carried out by conducting a routine sampling and analysis program for pelagic crude oil residues in coastal waters of west Florida. The program was designed not only to give an advance warning of impending danger, but also to recognize and identify any polluting oil. Special emphasis was placed on the detection of oil from IXTOC-I.

Surface Circulation in the Gulf of Mexico

The IXTOC-I blowout demonstrated the need for state and federal agencies to have the best available knowledge of surface water circulation patterns in the Gulf of Mexico. In November, 1979, the State of Florida contracted Geo-Marine, Inc. (Richardson, TX) to predict where and when oil from the IXTOC-I blowout could impact coastal waters of Florida. Much of the surface water circulation information presented below comes from the final report prepared by Geo-Marine, Inc. (1980) for the State of Florida.

Surface circulation in the Gulf of Mexico is generally thought to be dominated by two circulation patterns. The eastern Gulf is dominated by the presence of the Loop Current, which enters the Gulf of Mexico via the Yucatan Straits and exits through the Florida Straits, joining the Gulf Stream in the North Atlantic. The circulation in the western Gulf of Mexico is less clear, and there is still controversy as to whether the circulation is dominated by wind stress or by eddies breaking off of the Loop Current and forming a large anticyclonic gyre in the western Gulf. Offshore winds across the entire Gulf are easterly year-round. The primary seasonal changes observed are due to the passage of cold fronts and tropical storms through the Gulf. These noneasterly episodes are generally of short duration and do not significantly alter the average yearly circulation pattern. Nonetheless, they do provide an opportunity for breaking down the normal circulation patterns in the Gulf.

Data collected on wind, Loop Current, and drifter studies have led Geo-Marine to propose four zones of circulation in the Gulf of Mexico (Fig. 1). The central western Gulf (Zone 1) is dominated by an anticyclonic gyre generated by a coupling of wind and Loop Current circulation vectors. The alongshore currents and onshore–offshore water movement in the northwestern Gulf are highly variable and not well understood. The Bay of Campeche defines the boundaries of Zone 2 which contains a cyclonic gyre that expands and contracts depending upon changing wind conditions. The Loop Current in the eastern Gulf of Mexico (Zone 4) is much better defined but is still highly variable in lateral extent and volume flow. No correlation between the intrusion of the Loop Current into the Gulf with season was discerned in the Geo-Marine study. It is well documented, however, that the Loop Current makes periodic intrusions northward onto the west Florida shelf and westward of the Yucatan Straits, and it can then entrain material transported from the western Gulf of Mexico. Zone 3 is a transition zone between Zones 1 and 4 with no well defined circulation pattern. On an annual basis, very little exchange would be expected between adjacent zones. As mentioned above, however, short term circulation anomalies can be expected.

The observed distribution of surface oil released from IXTOC-I during August and September, 1979 (Fig. 2A)

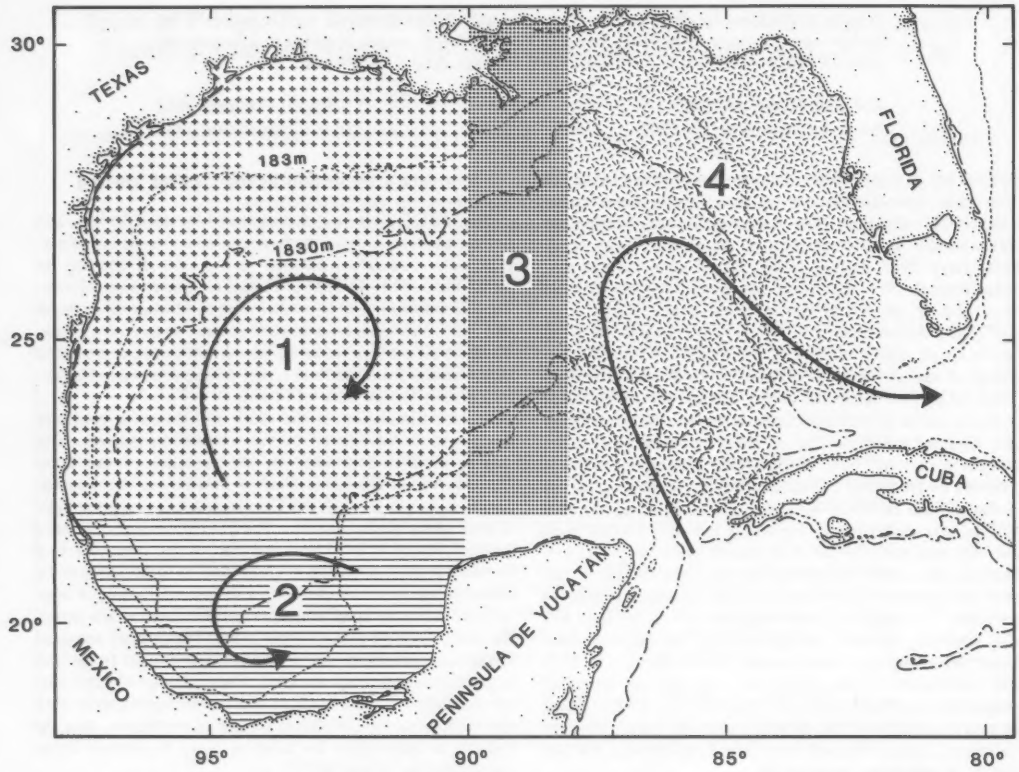

FIG. 1. The four surface current circulation zones of the Gulf of Mexico based on studies of wind, Loop Current, and drifter data (after Geo-Marine 1980).

represents the easternmost transport of visually recognizable amounts of IXTOC-I oil; penetration of the oil from Zone 2 through Zone 1 and into Zone 3 has occurred. It is apparent that entrainment of IXTOC-I oil by the Loop Current (Fig. 2B) with subsequent transport of the material into the eastern Gulf was possible under conditions prevailing in July and November. Although the possibility for transport of pelagic tar from the western to eastern Gulf of Mexico has been demonstrated, Geo-Marine (1980) concludes that the probability of this transport occurring is extremely low.

Sampling Strategies and Procedures

Pelagic tar concentrations were measured for samples collected monthly in the eastern Gulf of Mexico over a 1-yr period. Samples were collected along two standard transects of seven stations each. The two transects, of approximately 480 km each, were designed to intercept the Gulf Loop Current and detect entrained oil residues along the entire western Florida coastline (FIO/USF 1981). One transect ran from Tampa Bay southwest toward the Yucatan Peninsula; the other transect ran from Tampa Bay northwest toward the Mississippi Delta region. The seven stations along each transect were located at standard intervals and were selected so that the outer four stations in each case were in the Loop Current while the inner three stations were in coastal or marginal shelf waters. The two standard tracks were originally designed to be occupied alternately, each on a bimonthly basis to insure that sampling would reflect the influx of current-borne oil residues in the Loop Current, regardless of the time of year. As variability in pelagic tar concentrations, Loop Current intrusions, and temporal tar variations became apparent throughout the year, this sampling pattern was adjusted to insure intersection with the prevailing Loop Current and to maximize detection of entrained oil.

Satellite imagery from the NOAA Geophysical Oceanographic Environmental Satellite (GOES) was made available by the National Environmental Satellite Service in Miami. Surface temperature information from the GOES satellite was monitored routinely to determine the location of the Gulf Loop Current. When Gulf waters became homogeneous in temperature with Loop Current water (July–September), the position of the Loop Current could no longer be determined

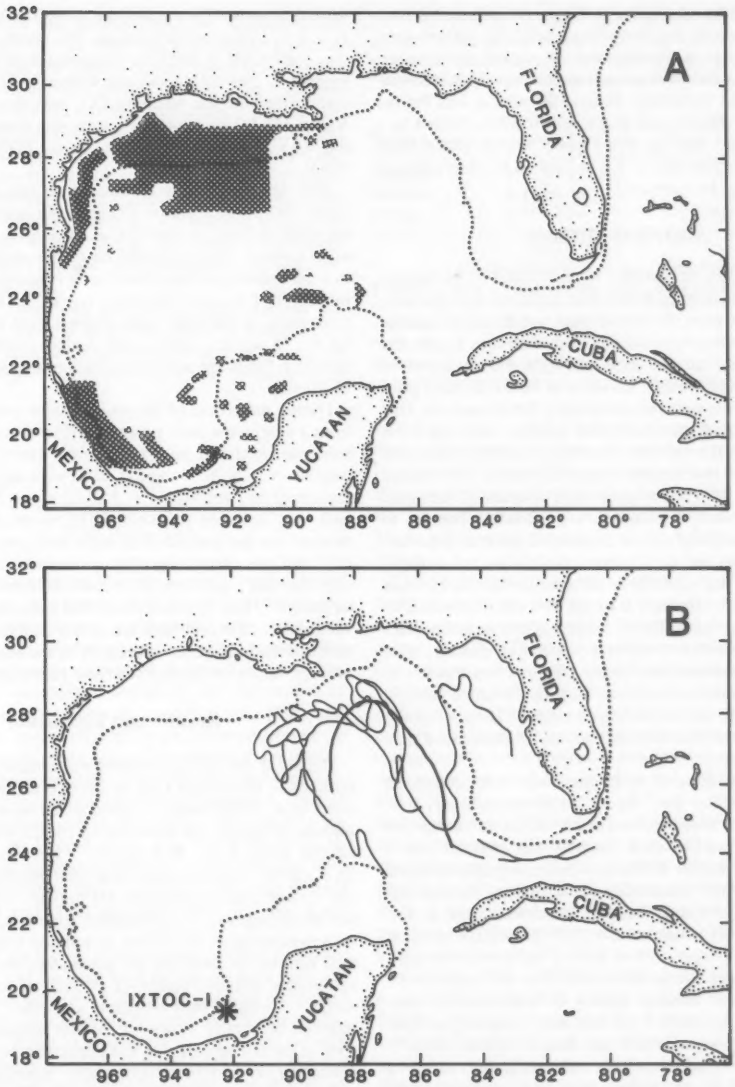

FIG. 2. (A) Distribution of surface oil material during the combined months of August and September 1979; (B) Positions of the Gulf Loop Current axis for combined months of July and November 1979 (after Geo-Marine 1980).

from the satellite data. Shipboard XBT temperature data were then used to determine the position of the Loop Current. Salinity and temperature profiles of the water column at each station were obtained for water mass characterization using a Plessey Model 9060 STD unit. The Gulf Loop Current was identified by the presence of the 22° isotherm at 100 m (Nowlin 1971; Maul 1977).

Pelagic tar was collected using a 1.5 m × 0.5 m neuston net designed after Morris (1971) and equipped with a TSK flow meter to monitor the water volume passing through the net. The nylon neuston net had a mesh size of 165 μm, a scope of 5:1, and was towed approximately 50 m off the starboard side of the R/V *Bellows* at 2–3 km/h for 10–30 min. In this manner, 500–1000 m^3 of seawater were

filtered through the nets during each tow. At each station, two surface neuston tows and two oblique tows (0−100 m) were taken for analysis of floating and suspended tar residues. Duplicate tows were taken at each station to provide information on sampling variability. Pelagic tar passing into the net was channeled into the cod end where it was collected in a 0.95-L glass jar. The jar was capped with a Teflon-lined screw cap and refrigerated at 5°C or kept on ice until returned to the laboratory for analysis.

Analytical Methods

After the pelagic tar samples were returned to the laboratory, tar particles from each tow were removed from the jars, weighed (to determine the wet weight), and dissolved in toluene to form a homogenous sample from each tow. In selected instances, the wet tar was dried overnight and reweighed to determine moisture content. All solvents were redistilled prior to use, and controls were run periodically for all analysis. One to 2 mL aliquots of the toluene/tar solution were taken for determination of the toluene extractable material, molecular characterization, and isotopic characterization. The toluene was evaporated from one aliquot under a stream of nitrogen, and the sample was weighed on a top loading balance to determine the weight of toluene extractable material in the tar. The sample used for hydrocarbon molecular and isotopic characterization was saponified, extracted, evaporated to near dryness and passed through a 10 cm × 1 cm diameter activated silica gel column. The F_1 (aliphatic hydrocarbon) fraction was eluted with two column volumes of hexane; after which, the F_2 (aromatic hydrocarbon) fraction was eluted with two column volumes of toluene. Each hydrocarbon fraction was evaporated to dryness in a preweighed Teflon weighing boat and the F_1 and F_2 hydrocarbon weights determined on a microgram balance.

The molecular nature of the hydrocarbons was determined for each fraction by gas−liquid chromatography. Hydrocarbon extracts were redissolved in 20−30 μL of hexane and approximately 1 μL of each fraction was injected into a Hewlett-Packard Model 5880A gas chromatograph equipped with a 12 m SP2100 fused silica glass capillary column and flame ionization detector. Running conditions were as follows: injection port temperature = 225°C; splitless injection mode; detector temperature = 250°C; column oven temperature programmed from 100 to 255°C at 4°C·min^{-1}; carrier gas = helium; column flow = 0.78 mL·min^{-1}; auxillary make up gas flow = 30 mL·min^{-1}; hydrogen flow = 30 mL·min^{-1}; compressed air flow = 420 mL·min^{-1}. Chromatograms were recorded and integrated using a Hewlett-Packard Level 4 data processor equipped with BASIC programming capability. Data obtained from the chromatograms included percent resolved components, percent unresolved components, nC$_{17}$/pristane, nC$_{18}$/phytane, pristane/phytane, n-alkane range, n-alkane maximum, and aromatic range.

The stable carbon isotopic compositions, expressed in terms of δ^{13}C where

$$\delta^{13}\text{C (in ‰)} = [(^{13}\text{C}/^{12}\text{C sample})/(^{13}\text{C}/^{12}\text{C standard}) - 1] \times 1000$$

were determined for the total tar as well as for the individual F_1 and F_2 hydrocarbon fractions. The residue of each sample was combusted at 500°C in the presence of CuO in a sealed ampule to convert the organic matter to CO_2. The isotopic composition of the resulting CO_2 was determined using a Varian MAT 250 isotope ratio mass spectrometer. Readout of the MAT 250 was directly in ‰ vs. the PDB standard (Craig 1953).

The detection limits for the hydrocarbon analyses were about 150 μg of aliphatic and aromatic hydrocarbons (twice the blank values). In virtually all cases these corresponded to approximately 10 mg of total tar (wet weight). This resulted in a minimum detectable floating tar concentration of approximately 0.01 mg·m^{-3} (i.e. 0.01 μg·L^{-1}). Dissolved tar concentrations in the Gulf Loop Current have been reported of up to 75 μg·L^{-1} (Iliffe and Calder 1974). Hence, our detection limits are well below background levels in the Gulf of Mexico.

During the course of the project, three individual tar balls from a single tow were processed. The remaining tar in that tow was analyzed in batch form. Three tar balls (wet weights = 0.20, 0.21, and 0.20 g) were separated from the remaining tar (wet weight = 5.25 g) in tow S1180-4N2[3] and each was analyzed separately. The results from this study showed that the individual tar balls were very similar in their δ^{13}C and gas chromatographic parameters. All three, however, showed significant differences from the remaining bulk tar sample. These results indicate that there may be significant variations within each bulk tar sample analyzed. The bulk tar samples reported for the remainder of the study represent the average values of the characteristic parameters measured.

Results and Discussion

Details of the spatial and temporal variations of pelagic tar residues in the eastern Gulf of Mexico can be found in Van Vleet et al. (1982) and are summarized below. The concentrations of pelagic tar observed in coastal waters of Florida ranged from 0 to 45.3 mg·m^{-2} wet weight and 0 to 26.5 mg·m^{-2} toluene extractable lipid material (overall average surface concentration of 1.01 mg·m^{-2}). The floating tar had an average moisture content of approximately 59 ± 21% (observed range = 19−97%). In addition to the water associated with the tar particles, the remainder consisted of toluene extractable organic matter ($\bar{x} \simeq 35\%$ of the wet weight; range = 0−86%) plus inorganic and other organic detrital material (generally 1−3% of the wet weight). Thus, about 95% of the dry tar particles was extractable with toluene. The concentration of toluene extractable material found in the oblique tows (0−100 m) ranged from 0 to 0.20 mg·m^{-2} with an average of 0.01 mg·m^{-2} (Table 1). Pelagic tar found in the eastern Gulf of Mexico is primarily associated with the Gulf Loop Current. Tar concentrations found in neuston tows taken

[3]Cruises are designated by direction of transect (S=Southern, N=Northern) plus month and year (example: S1180=Southern transect, November 1980). Individual tows are designated by station, type of tow (N=Neuston, OB=Oblique), and replicate 1 or 2 (example: 4N2=Station 4 Neuston tow 2).

off the west Florida continental shelf, i.e. stations which roughly correspond to the Gulf Loop Current, averaged 1.60 $mg \cdot m^{-2}$, while tar concentrations found on the shelf averaged only 0.05 $mg \cdot m^{-2}$ (Table 1). Tar collected from stations along the northern transects (which are also primarily on the Florida continental shelf and outside the Loop Current) showed concentrations similar to the stations on the continental shelf from the southern transects. These concentrations are much lower than the tar associated with the Loop Current. For the southern transects, the average pelagic tar concentration was highest during the May 1980 cruise (4.6 ± 7.3 $mg \cdot m^{-2}$) and decreased throughout the summer, fall, and winter months.

A method for classifying pelagic tar concentrations has been proposed by Wong et al. (1976) based on samples collected in the Pacific Ocean. These authors arbitrarily assigned the following designations to the floating tar concentrations (wet weights):

No visible tar	≡ Zero (0)
<0.1 $mg \cdot m^{-2}$	≡ Trace (T)
$0.1-1$ $mg \cdot m^{-2}$	≡ Medium (M)
$1-5$ $mg \cdot m^{-2}$	≡ Heavy (H)
>5 $mg \cdot m^{-2}$	≡ Extra Heavy (X)

This classification procedure has subsequently been used by other authors (Shaw and Mapes 1979; Eagle et al. 1979) and provides a convenient means of comparing pelagic tar data from different areas. Based upon this classification, the pelagic tar concentrations observed during Year 1 of the present study are summarized in Fig. 3. The distribution of pelagic tar is extremely patchy. As a result of this patchiness, there is certainly some overlap in the contours shown in Fig. 3. The contours more accurately represent the probability of finding trace, medium, heavy, or extra heavy pelagic tar concentrations in various sectors of the eastern Gulf of Mexico. If the contour curves (Fig. 3) are compared to the expected axis of the Loop Current (Fig. 1 and 2), it can be seen that heaviest tar concentrations again correlate with the Loop Current while the stations on the west Florida continental shelf (<183 m) generally show the lowest tar concentrations.

In the present study, the stable carbon isotopic compositions were measured for each total tar sample plus each aliphatic (F_1) and aromatic (F_2) fraction. In addition, the F_1 and F_2 fractions were also analyzed by gas–liquid chromatography. Thus, five different analyses were performed on each tar sample collected. In this manner, problems associated with differential weathering of the tar components during the days, weeks, or months of transport to the eastern Gulf were minimized.

A total of 265 tows were taken during the study. Of these tows, 109 (41%) contained pelagic tar. The size of the individual tar particles ranged from about 165 μm to approximately 4.5 cm in diameter. Most fell in the range of 0.5–5 mm. The consistency of the tar varied from hard and crusty to soft and sticky. Colors varied between brown, grey, and black. Full details of the chemical data can be found in FIO/USF (1981).

Crude oils exhibit a wide range of characteristic $\delta^{13}C_{PDB}$ values (−22 to −35‰) that can often be used to differentiate various crude oil types (Kvenvolden and Squires 1967; Degens 1969; Stahl 1977). $\delta^{13}C_{PDB}$ values of the aliphatic and aromatic fractions of crude oils also vary between oils, and can be used in conjunction with the $\delta^{13}C_{PDB}$ value for the whole oil to give a more sensitive indicator of crude oil source.

TABLE 1. Average pelagic tar concentrations (expressed in $mg \cdot m^{-2}$ of toluene extractable lipid ± standard deviation) observed in neuston and oblique tows (after Van Vleet et al. 1982).

Transect	(I) Concentration in neuston tows (all stations)	(II) Concentration in oblique tows (all stations)
Southern	1.33±3.81	0.02±0.01
Northern	0.13±0.35	0.00±0.00
Overall	1.01±2.94	0.01±0.01

Transect	(III) Concentration in neuston tows on west Florida shelf	(IV) Concentration in neuston tows off west Florida shelf
Southern	0.06±0.08	2.07±3.16
Northern	0.02±0.06	0.19±0.32
Overall	0.05±0.08	1.60±2.45

The stable carbon isotopic values for the total tar samples analyzed during the present study averaged −27.2‰ with the F_1 fractions averaging −27.5‰ and the F_2 fractions averaging −27.0‰ (Table 2). Since there were likely to be several sources, as well as several transport and weathering mechanisms, for the pelagic tar, the average values found for each chemical parameter are not indicative of the variety of tars present. Each tar fraction showed a unimodal distribution that approximated a normal distribution around the mean. In the case of the total tar, approximately 74% of the samples had $\delta^{13}C_{PDB}$ values between −26.5 and −28.0‰. For the F_1 fractions, approximately 73% of the samples had $\delta^{13}C_{PDB}$ values between −27.0 and −28.5‰; the F_2 fractions had approximately 62% of the samples with a $\delta^{13}C_{PDB}$ value between −26.5 and −27.5‰. Generally, the $\delta^{13}C$ values for the F_1 fractions were more negative than the F_2 fractions with the total tar samples being intermediate. This trend did not hold for all the samples, however.

Similarly, there was wide scatter in the range of gas chromatographic parameters shown in Table 2. Approximately 70% of the samples showed an *n*-alkane maximum falling within the range of $C_{19}-C_{20}$ or $C_{29}-C_{35}$. According to Butler et al. (1973), crude oil sludge (i.e. tanker wall washings) is characterized by a bimodal distribution in the envelope of *n*-paraffin peaks. One maximum occurs at approximately C_{17} while the other maximum is at approximately C_{29}. Crude oils from normal operations, tanker accidents, or natural seeps do not show this bimodal *n*-paraffin distribution. In the pelagic tar samples investigated during this study, approximately 40% showed a bimodal distribution with the *n*-alkane maxima occurring in the $C_{19}-C_{20}$ and the $C_{29}-C_{35}$ ranges. Approximately 60% of the samples showed a unimodal distribution of *n*-alkanes with the maxima varying from C_{18} to C_{38}. In addition, a few of the chromatograms of the tar samples appeared similar to chromatograms of refined (Bunker C) oils. These

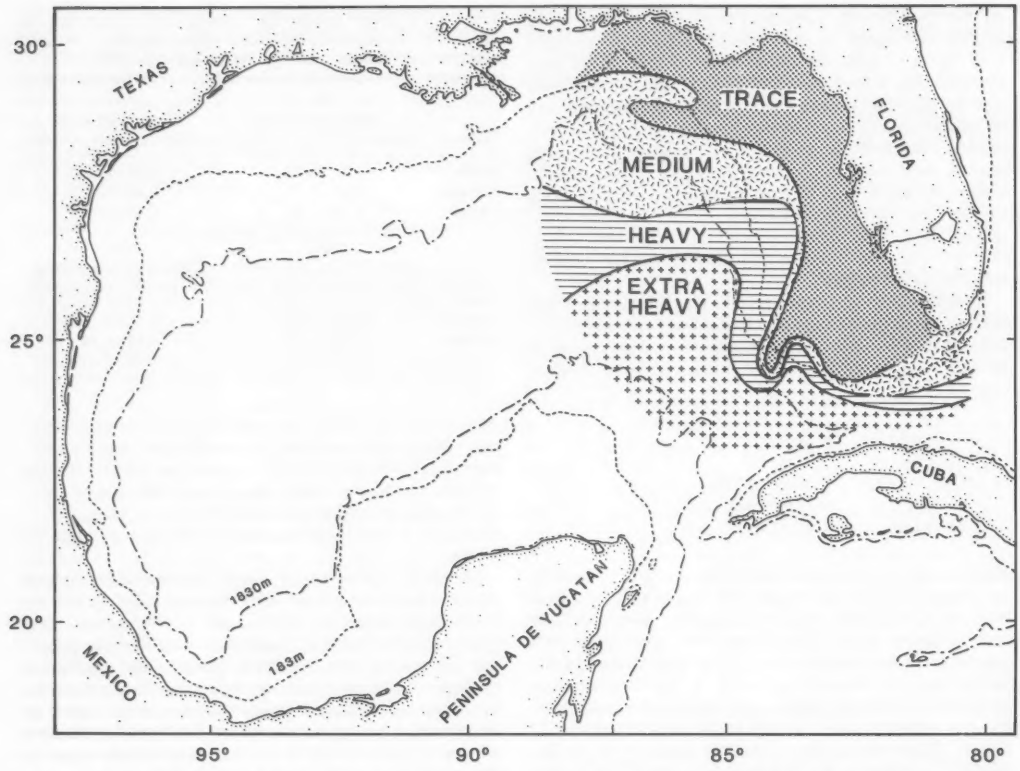

FIG. 3. Average distribution of surface tar in the eastern Gulf of Mexico, April 1980 through March 1981. Based upon the classification scheme of Wong et al. (1976). See text for equivalent wet weights.

results suggest that tanker operations are a prime contributor to the pelagic tar found in the eastern Gulf of Mexico. On the other hand, Koons and Monaghan (1973) used gas chromatographic and isotopic characterization to analyze pelagic tar collected off the coast of Texas and suggest that these hydrocarbons are derived primarily from natural seeps.

Much of the early, but definitive, work on weathering of crude oils was conducted by Ehrhardt and Blumer (1972). These authors found the following trends to hold for most crude oils. The early stages of weathering on an oil released into the sea are dominated by evaporation and dissolution, resulting in a rapid loss of lower molecular weight *n*-alkanes, isoalkanes, cycloalkanes, and aromatics up to about C_{14}. After the initial rapid loss of lower molecular weight components, dispersion (propulsion of oil droplets into the water column by breaking waves) microbial and chemical (photo/autooxidation) degradation and sedimentation become the dominating processes in determining the fate of the residual oil. Chemical degradation is not well understood but may approach microbial degradation in importance. During microbial degradation, normal alkanes are degraded first, followed by isoalkanes, cycloalkanes, and aromatics. The ratios of *n*-alkanes to isoprenoid compounds (i.e. nC_{17}/pristane and nC_{18}/phytane) are among the most diagnostic characteristics of microbial degradation of crude oil residues. The critical factor in applying these generalizations to the weathering of a specific oil is in understanding the rates at which these processes are occurring.

Haegh and Rossemyr (1980) investigated the weathering of IXTOC-I crude oil from the time it was released into the water column 38 m below the surface until it washed up on Texas beaches 2 mo later. Their results indicated that the loss from evaporation and dissolution of oil from a well blowout is approximately 70% and that after 2 mo, most of the evaporation and dissolution of the oil had taken place. Microbiological effects had begun prior to the IXTOC-I oil washing upon the Texas beaches, but these effects had been minor. Butler et al. (1973) found that tar balls can retain their characteristic molecular component ratios for several months after initial weathering losses.

From these studies, we can infer that if oil from the IXTOC-I blowout were to impinge on the coastal waters of western Florida after April, 1980 (10 mo after the well blowout and 1 mo after the flow had been shut off completely), any

TABLE 2. Chemical parameters observed in pelagic tar collected in the eastern Gulf of Mexico, April 1980 − March 1981.

Parameter measured	Range	Average ± standard deviation	Weathered IXTOC-I tar ball
$\delta^{13}C$ (total) ‰	−26.5−−28.0	−27.2±0.8	−27.3−−27.6
$\delta^{13}C$ (F_1) ‰	−26.3−−29.9	−27.5±1.4	−27.5−−27.8
$\delta^{13}C$ (F_2) ‰	−25.4−−29.6	−27.0±1.1	−26.9−−27.0
Aliphatics/aromatics	0.68−7.33	2.69±1.63	1.96
nC_{17}/pristane	0.14−4.60	1.54±0.79	3.20
nC_{18}/phytane	0.31−5.21	1.92±0.99	2.42
Pristane/phytane	0.41−2.79	1.00±0.38	0.39
n-Alkane range	C_{12}−C_{38}	C_{14}−C_{38}	C_{13}−C_{36}
n-Alkane maximum	C_{18}−C_{38}	C_{19}−C_{20};C_{29}−C_{35}	C_{18}−C_{21}
% resolved F_1	33.4−94.7	40.2±15.4	42.4±8.1
% unresolved F_1	5.3−71.4	59.8±15.4	57.6±8.1
% resolved F_2	7.9−45.6	25.4±13.8	32.0±7.9
% unresolved F_2	55.4−92.1	74.6±13.8	68.0±7.9

differences between the oil collected on the west Florida shelf and the oil that washed up on the beaches of Texas would primarily result from microbiological degradation processes and not from further dissolution or evaporation. The microbiological effects would be crudely predictable from Ehrhardt and Blumer's work (1972). The ratios of aliphatic/aromatic hydrocarbons would decrease as would the nC_{17}/pristane and nC_{18}/phytane ratios. The pristane/phytane ratios, the *n*-alkane range, and the *n*-alkane maximum would change very little, while the range of aromatic hydrocarbons might decrease slightly due to a small amount of further dissolution.

Representative chromatograms of the aliphatic fractions of pelagic tar samples collected during the study varied greatly (Fig. 4). The nC_{17}/Pr and nC_{18}/Py ratios are indicative of microbial degradation of the oils. In Fig. 4A, very little microbial degradation is apparent (e.g. high C_{17}/Pr and C_{18}/Py ratios of 2.11 and 3.36, respectively). Lower ratios (nC_{17}/Pr = 1.22; nC_{18}/Py = 1.26) in Fig. 4B indicate more microbial activity may have occurred in this sample. In Fig. 4C, the very low ratios (nC_{17}/Pr = 0.35; nC_{18}/Py = 0.32) indicate that extensive microbial activity may have occurred in the tar ball. Hence, sample A appears to be a relatively fresh tar, sample C a highly altered tar, and sample B an intermediate tar. Different source material could also account for this trend.

With these weathering considerations in mind, we attempted to compare the pelagic tar that was collected on the west Florida shelf to pelagic tar that washed up on the beaches of South Padre Island, Texas, approximately 2 mo after the spill. During the early stages of the project, we also analyzed fresh oil collected from the IXTOC-I well site during the June 1979 blowout (oil provided by the University of Texas). Based upon the stable carbon isotopes and gas chromatographic analyses of the IXTOC-I oil, our analytical procedures gave results which were virtually identical with those provided by the University of Texas. The weathering patterns of the IXTOC-I oil have been reported by Parker et al. (1979) and are described in Table 2. These values are similar to those reported for weathered IXTOC-I tar by Boehm and Fiest (1980), Botello and Cástro-Gessner (1980), and Sweeney et al. (1980). Using a combination of molecular characterization and $\delta^{13}C$ isotopic characterization, determination of the similarity of the collected tar to weathered IXTOC-I oil was attempted. In comparing our carbon isotope results to the weathered IXTOC-I values, the ranges obtained for weathered IXTOC-I tar ± 0.5‰ were used to determine similarity or dissimilarity. Likewise, the gas chromatographic data on the weathered IXTOC-I tar samples was interpreted quite liberally to allow for more or less weathering of the tar during its transport to the west Florida shelf. By taking this approach to the weathered IXTOC-I values, we can be reasonably certain that tar samples falling outside of the similarity limits do not come from the IXTOC-I blowout. If the similarity comparison parameters are taken individually, approximately half of the oil produced in the Gulf of Mexico can fall within the given limits. Taken collectively, however, the parameters can be used to give a reasonable indication of the similarity of the pelagic tar collected in this study to that released during the IXTOC-I blowout. When taken individually, several of the whole tar, F_1, or F_2 samples had $\delta^{13}C$ values similar to the values found in weathered IXTOC-I tar. Taken collectively, however, the values for most samples were not representative of IXTOC-I tar. Similarly, chemical characterization by gas−liquid chromatography showed that most of the tar balls collected on the west Florida continental shelf had a different molecular nature than expected for weathered IXTOC-I tar. Although several of the pelagic tar samples showed some characteristics of the IXTOC-I oil, very few could not be completely distinguished from the IXTOC-I oil. Out of 109 stations where measurable pelagic tar was collected, only 15 of the samples (14%) could not be distinguished from weathered IXTOC-I oil. Eight of the cruise transects contained 0, 1, or 2 samples that resembled the IXTOC-I oil. Only two of the transects had a slightly higher number of stations containing IXTOC-like tar (S680: $n = 5$; N880: $n = 4$). Thus it does not appear that large amounts of IXTOC-I oil have impinged on coastal waters of Florida, but rather that there may be a small background of IXTOC-like oil present, over which are superimposed larger amounts of oil from other origins. Cordes et al. (1980) and Romero et al. (1981) reached similar conclusions based upon pelagic tar and beach tar samples collected around Georgia and Florida.

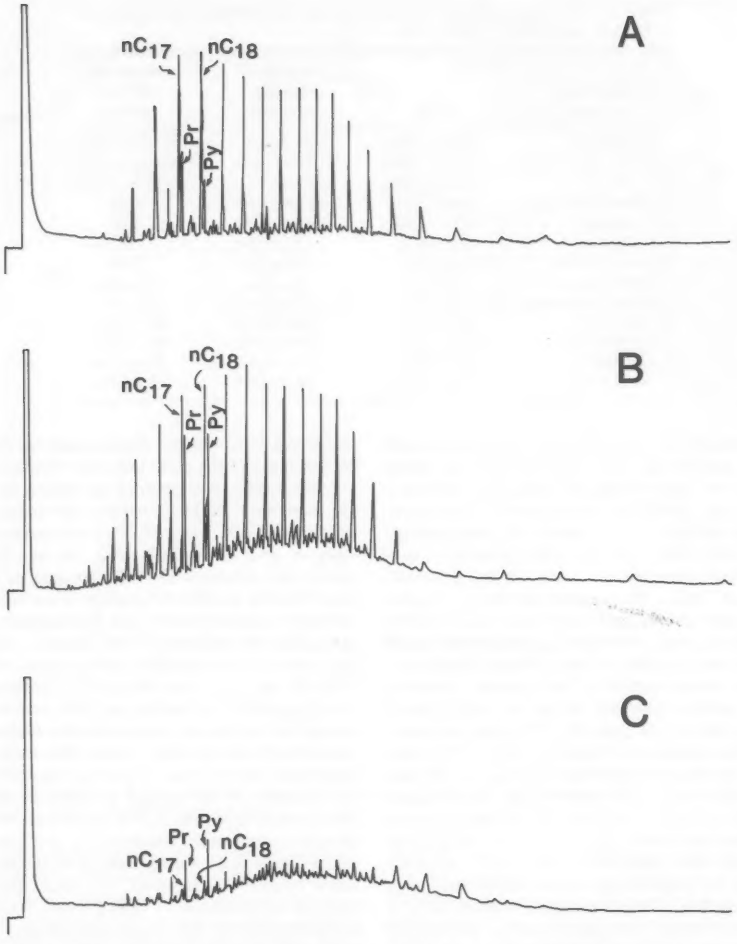

FIG. 4. Representative gas chromatograms of the aliphatic fractions of tar balls collected from the west Florida continental shelf. Cruise numbers: A=S480-1N2; B=S480-6N2; C=S480-60B1. Pr=pristane; Py=phytane; nC_{17}=hyptadecane; nC_{18}=octadecane.

According to Leipper (1970) and Nowlin (1971), penetration of the Loop Current into the eastern Gulf varies seasonally, with maximum flow usually occurring in the late summer to early fall. Occasionally, particularly in winter months, the Loop may pinch off and form a gyre which then begins to decay and spread into the western Gulf. Average Loop Current volume through the Yucatan Channel is 25–30 $\times 10^6$ $m^3 \cdot s^{-1}$; current velocities at the surface near the edge of the Loop reach 200 $cm \cdot s^{-1}$ (Leipper 1980; Jones 1973). The effective depth of the Loop Current roughly coincides with the thermocline depth of 200 m. The only other principal water flow into the Gulf of Mexico is the Mississippi River, which has only 0.1% of the flow of the Loop Current (estimated average = 0.07×10^6 $m^3 \cdot s^{-1}$; Turekian 1971; Jones 1973; LaRock and Bittaker 1973). This water input to the Gulf is negligible compared to the input from the Loop Current. The average tar concentration observed in the upper 0.5 m of the Loop Current over the 1-yr study period was 1.60 $mg \cdot m^{-2}$. This corresponds to an average surface water concentration of 3.20 $mg \cdot m^{-3}$ for the top 50 cm. Quantities of pelagic tar occurring from 50 cm to 200 m are considered negligible. If the water input from the Mississippi River is also considered negligible, the average surface water discharge (to 50 cm) through the Florida straits is approximately the same as the input through the Yucatan Channel, i.e. $6.2–7.5 \times 10^4$ $m^3 \cdot s^{-1}$. Using an average tar concen-

tration of 3.20 $mg \cdot m^{-3}$ yields an annual discharge from the Gulf Loop Current to the North Atlantic of 6.3 to 7.6 $\times 10^3$ t (average $\simeq 7.0 \times 10^3$ t) of pelagic tar. It should be emphasized that this represents a yearly average discharge and does not account for seasonal variations in tar input or Loop Current flow.

Certainly a large percentage of the pelagic tar in the Loop Current is carried in from the Caribbean Sea through the Yucatan Channel. Jeffrey et al. (1974) reported an average pelagic tar concentration in the Caribbean Sea of 0.74 $mg \cdot m^{-2}$ (toluene extractable material), significantly below the levels found in the Gulf Loop Current. Average concentrations reported for the western Gulf of Mexico, however, range from 1.20 $mg \cdot m^{-2}$ (Jeffrey et al. 1974) to 1.58 $mg \cdot m^{-2}$ (from Pequegnat 1979, assuming 95% of the dry tar weight is toluene extractable). These values are similar to the values found in the Loop Current during this study. It therefore seems likely that there are significant additional inputs of pelagic tar in the Gulf of Mexico. Despite the fact that the Mississippi River has a flow which is only 0.1% of that of the Loop Current, it has a disproportionate impact on the Gulf in terms of nutrient and suspended matter transport (LaRock and Bittaker 1973). Most of the Mississippi discharge occurs in the spring (March–May), and surface current and salinity patterns indicate that runoff flows into both the eastern and western Gulf (Nowlin 1972; LaRock and Bittaker 1973; Maul 1974). Hence, the Mississippi River may account for a significant contribution of pelagic tar in the Gulf of Mexico. Other significant sources of pelagic tar in the Gulf may include production and tanker operations in the Gulf of Mexico and major accidental discharges such as the IXTOC-I blowout in June 1979.

At the present time, we do not have an adequate measure of pelagic tar entering the Gulf of Mexico through the Yucatan Channel. If we assume that the average concentration of tar coming in is the average concentration observed by Jeffrey et al. (1974) in the Caribbean Sea (0.74 $mg \cdot m^{-2}$), the average concentration found in the Loop Current during the present study (1.60 $mg \cdot m^{-2}$) is approximately double the amount entering the Gulf via the Yucatan Channel. Hence the amount of tar added to the Loop Current by sources in the Gulf of Mexico is estimated to be approximately 3500 $t \cdot yr^{-1}$. This also represents the amount of tar recycled from the Caribbean, through the Gulf of Mexico to the Atlantic via the Gulf Loop Current. The accuracy of this estimate awaits further investigation of the actual concentrations of pelagic tar entering through the Yucatan Channel.

Acknowledgments

Financial support for this project was provided by the Florida Coastal Protection Trust Fund and the Florida Department of Natural Resources. We are especially grateful to Vice-Admiral W. W. Behrens Jr. and Mr D. M. Milliken of the Florida Institute of Oceanography, as well as the Captain and crew of the R/V *Bellows*, for logistical and sampling support. We sincerely appreciate the efforts of Dr Karen Steidinger, Director of the Florida Department of Natural Resources Bureau of Marine Science and Technology. Crude oil collected from the IXTOC-I well site, as well as data on weathered IXTOC-I particles were provided by Drs P. L. Parker, R. S. Scalan, and J. K. Winters of the University of Texas Marine Science Institute.

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Baseline Levels of Volatile Hydrocarbons and Petroleum Residues in the Waters and Sediments of the Grand Banks[1]

E. M. LEVY

Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

LEVY, E. M. 1983. Baseline levels of volatile hydrocarbons and petroleum residues in the waters and sediments of the Grand Banks. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 23–33.

Baseline levels of low molecular weight volatile hydrocarbons and petroleum residues in the Grand Banks area were measured in April 1981 with a focus on the Hibernia and South Tempest sites where exploration for oil was occurring. Concentrations of volatile hydrocarbons ranged from 0.41 to 1.80 nmol/L (geometric mean = 0.74 nmol/L) in the water column and 0.05–3.20 mmol/L in the surficial bottom sediments. The former, almost exclusively methane, were of recent biological origin, while the latter, which also contained ethane, propane, and butane, were probably related to petroleum. There was no visible evidence of surface slicks at the time, and floating particulate petroleum residues were absent from most locations. Concentrations of dissolved/dispersed petroleum residues in the sea surface microlayer ranged from 14 to 440 μg/L (geometric mean = 28.9 μg/L) and in the water column from 0.05 to 4.1 μg/L. Concentrations of petroleum residues in the surficial bottom sediments ranged from 0 to 7.3 μg/g. While these levels are among the lowest found anywhere in the waters and sediments off eastern Canada and in the eastern Arctic, there was evidence that the oil industry, even at the level of its activity at the time, was having a detectable impact on background levels of petroleum-related substances in the sea surface microlayer and the surficial bottom sediments.

LEVY, E. M. 1983. Baseline levels of volatile hydrocarbons and petroleum residues in the waters and sediments of the Grand Banks. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 23–33.

Les niveaux de base d'hydrocarbures volatils de faible poids moléculaire et de résidus de pétrole dans la région des Grands bancs ont été mesurés en avril 1981, plus particulièrement aux sites d'exploration pétrolière Hibernia et South Tempest. Les concentrations d'hydrocarbures volatils varient de 0,41 à 1,80 nmol/L (moyenne géométrique = 0,74 nmol/L) dans la colonne d'eau et de 0,05 à 3,20 mmol/L dans les sédiments superficiels du fond. Les premiers, presque exclusivement méthane, ont une origine biologique relativement récente, tandis que les seconds, contenant aussi éthane, propane et butane, sont probablement associés au pétrole. On n'a observé à cette époque aucune nappe superficielle et, à la plupart des sites, les résidus de pétrole particulaire flottant étaient absents. Dans la microcouche superficielle de la mer, les concentrations de résidus de pétrole dissous/dispersé varient de 14 à 440 μg/L (moyenne géométrique = 28,9 μg/L) et dans la colonne d'eau, de 0,05 à 4,1 μg/L. Dans les sédiments superficiels du fond, les concentrations de résidus de pétrole varient de 0 à 7,3 μg/g. Ces niveaux sont parmi les plus bas observés en aucun endroit dans les eaux et les sédiments au large de la côte est canadienne et dans l'Arctique oriental, et on n'a pas d'indication que l'industrie pétrolière, même au niveau d'activités de l'époque, influe de façon marquée sur les concentrations de base des substances associées au pétrole dans la microcouche superficielle de la mer et dans les sédiments superficiels du fond.

Received March 18, 1982
Accepted November 1, 1982

Reçu le 18 mars 1982
Accepté le 1 novembre 1982

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6842)
Imprimé au Canada (J6842)

EXPLORATORY drilling at the Hibernia and South Tempest sites has demonstrated commercially exploitable reserves of petroleum on the Grand Banks off Newfoundland (Fig. 1), and over the next few years the industry will continue its exploratory and delineation drilling in preparation for the production of oil from this region. It is inevitable that these

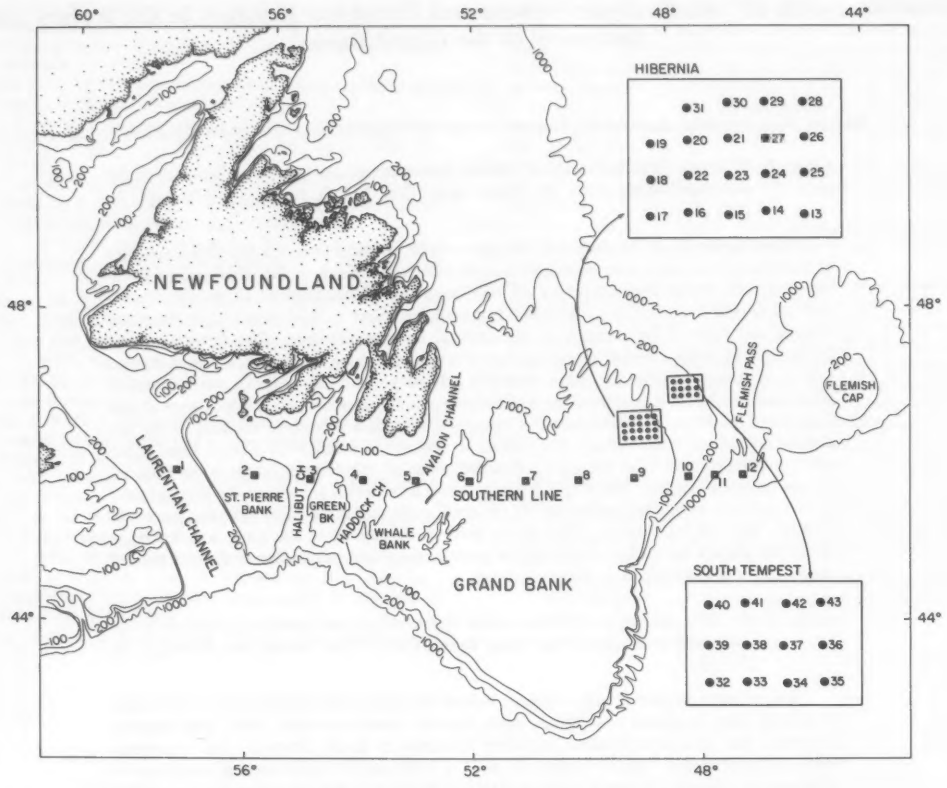

FIG. 1. General bathymetry of Grand Banks area and the locations of stations at which sampling was carried out.

activities will have some impact on the environmental quality of the Grand Banks, an area that supports one of the most important fisheries in the North Atlantic. Consequently, Canada has been confronted with the dilemma of obtaining the maximum benefit from the petroleum resource without undue detriment to the fishery. That these industries need not be mutually exclusive has been demonstrated in the North Sea, and accordingly, it should be possible for Canada to resolve the environmental, economic, and social conflicts that will ensue. However, this will only be possible if the appropriate scientific information is available so that sound policy decisions can be made. The first step with respect to the environmental quality component is to collect reliable data concerning existing levels of petroleum-related substances in the waters and surficial bottom sediments of the area. Although some of this information must be provided by the industry in its Environmental Impact Statement to comply with government requirements for granting licenses, it is essential that an independent data base be available also so that the reviewing agencies can assess the validity of the data supplied by the industry and its claims regarding the impacts of its activities on the marine environment. In addition, reliable information concerning the baseline levels of petroleum will undoubtedly be required at some time in the future to assess the cumulative effects of the day-to-day operations of the industry or the impact of a blow-out such as those that have already occurred in the North Sea and in the Gulf of Mexico. Accordingly, a survey of the Grand Banks area with a focus on the Hibernia and South Tempest sites was carried out April 7–17, 1981 (CSS *Dawson* cruise No. 81-008), to collect data concerning baseline levels of low molecular weight hydrocarbons and of dissolved/dispersed petroleum residues in the sea surface microlayer, the water column, and surficial bottom sediments.

Sampling and Analytical Methods

During this survey of a line of 12 stations (referred to as the southern line) extending from the Laurentian Channel across the Grand Banks to Flemish Pass and grids (9.3 km × 9.3 km) of 19 and 12 stations at the Hibernia and South Tempest sites, respectively, were sampled (Fig. 1). The strategy for this and

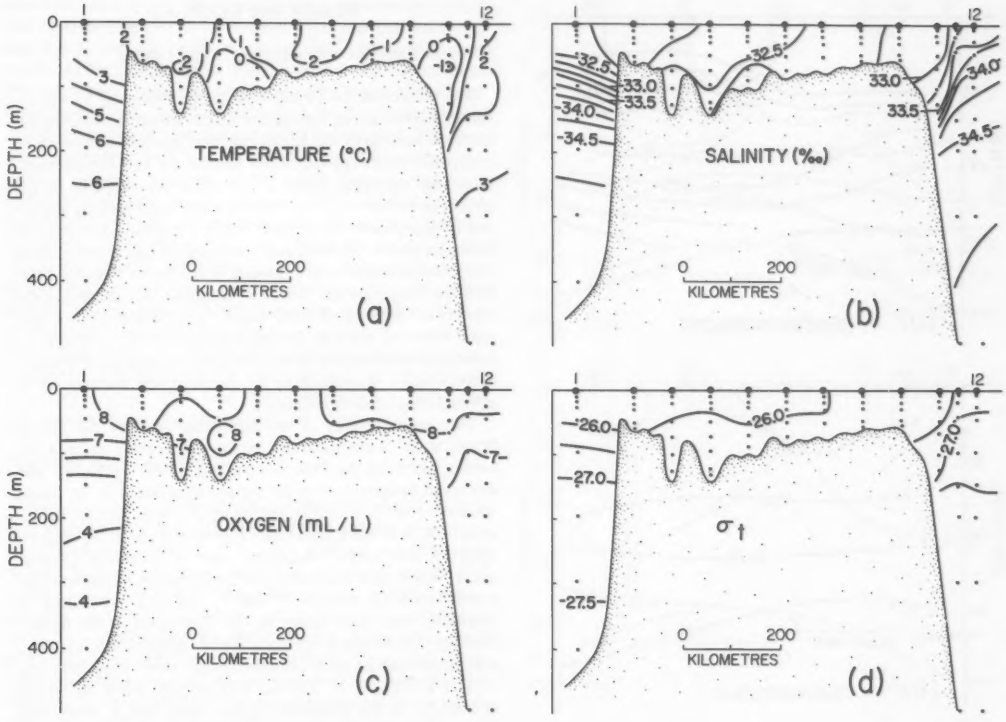

FIG. 2. Cross-sections showing (a) temperature, (b) salinity, (c) dissolved oxygen, and (d) σ_t along the southern line (April 7–17, 1981).

previous studies by this laboratory of the background levels of petroleum-related substances in areas of Canadian interest (Levy 1971, 1972, 1979a, 1981; Levy and Walton 1973) has been to use the simplest and most economical sampling and analytical procedures that are capable of yielding meaningful results to generate as extensive as possible a data base for a geographical region. Thus, it is not only possible to gain a measure of the background level and the local variability within the region but also to identify "hot spots" or other features that merit subsequent examination in greater detail using more dense sampling and more sophisticated methods of analysis including capillary gas chromatography/mass spectrometry for the identification and quantification of individual components. For these reasons and to ensure that the data for the Grand Banks would be compatible with our existing data base the methods of sampling and analyses used during this cruise were identical to those employed previously.

Water samples were collected from the surface microlayer using a modified version of the Garrett screen sampler (Garrett 1965) and throughout the water column using 5-L Niskin samplers on a CTD/Rosette assembly. This latter device generated continuous profiles of temperature and salinity as it was lowered to within a few metres of the bottom, and the samplers were closed at the standard oceanographic depths during retrieval. This procedure has previously been shown to avoid contamination from overlying waters and thereby provide reliable data concerning background levels of petroleum residues in the open ocean (Levy 1979b). Volatile hydrocarbons (C_1-C_6) in the water samples were extracted by equilibration with helium (McAuliffe 1971) and determined immediately by gas chromatography. Dissolved/dispersed petroleum residues were extracted with carbon tetrachloride and subsequently determined by ultraviolet fluorescence spectrophotometry (Levy 1977).

Surficial bottom sediments were collected using a clean Van Veen grab sampler. Duplicate subsamples were placed in glass jars for the immediate determination of volatile hydrocarbons by gas chromatography using a headspace technique and frozen for later analysis by fluorescence spectrophotometry.

Samples of floating particulate tar were collected by towing a neuston net (mesh size = 243 μm) for 1.9 km at 3 m/s (area sampled = approximately 740 m^2). These were analyzed gravimetrically (Levy and Walton 1973) and by high-temperature gas chromatography (Levy et al. 1973).

Visual observations of the sea surface according to the procedures of the IOC/WMO Pilot Project on Marine

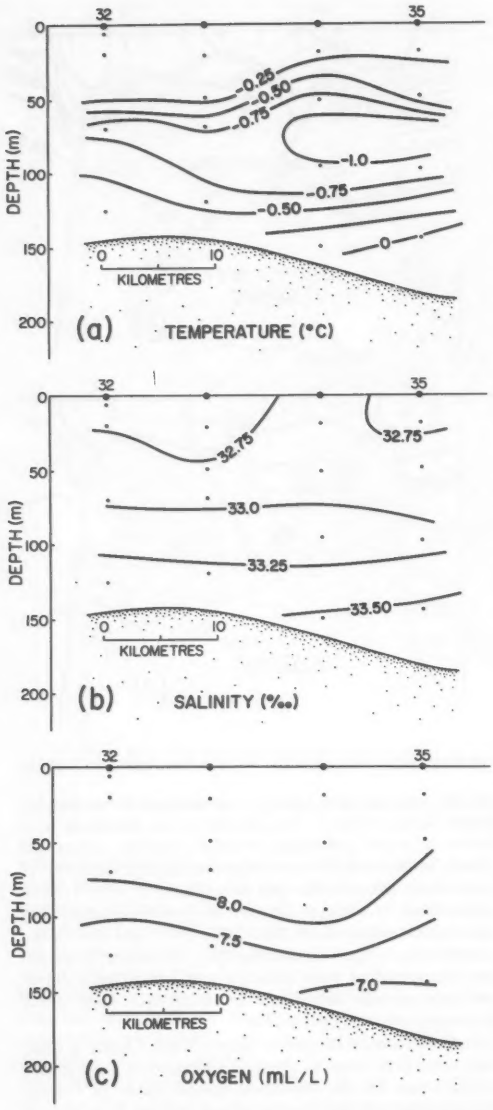

FIG. 3. Representative cross-sections showing (a) temperature, (b) salinity, and (c) dissolved oxygen data for South Tempest grid.

Pollution (Petroleum) Monitoring (Anonymous 1976) were made throughout the cruise to determine the distribution of oil present as surface slicks.

To provide ancillary oceanographic data, water samples were collected and analyzed for salinity, dissolved oxygen, and nutrients.

Results and Discussion

HYDROCHEMISTRY AND GENERAL CIRCULATION

The waters of the Grand Banks are dominated by the inshore portion of the Labrador Current which flows onto the northern portion of the banks and then spreads southward in a complex system of seasonally and locally variable currents. In spring, the upper layers of this water are modified by the annual influx of cold, low salinity water from melting sea ice and of freshwater from runoff along the Newfoundland and Labrador coasts. Warmer and more saline slope water present along the continental slope south of the banks intrudes from time to time onto the banks in response to meteorological conditions. Mixing of these waters in conjunction with seasonal warming accounts for the chemical and physical characteristics of the water in each of the areas studied and is a major consideration in accounting for the observed distribution of petroleum-related substances.

The main features of the hydrochemistry of the Grand Banks at 46° N are illustrated by the temperature, salinity (all values based on the Practical Salinity Scale 1978), σ_t, and dissolved oxygen sections for the southern line (Fig. 2). Slope water (>5.0°C, >34.5‰, <5.0 mL/L) was present below about 150 m in the Laurentian Channel and along the western slope of the banks whereas a core of Labrador Current water, which gave rise to the low temperatures throughout the water column at stations 10 and 11 and near the bottom at station 8, was found along the seaward slope of the banks. Over the Grand Bank (stations 5–9), temperature, salinity, and dissolved oxygen concentrations were very uniform (1.5 ± 0.5°C, 32 ± 0.25‰, 8.0 mL/L), while the small differences in the properties of the water east to west over Grand, Green, and St. Pierre banks reflected the admixture of differing proportions of modified Labrador Current water and slope water. For example, at station 4, which was directly in the flow of modified Labrador Current water through the Avalon and Haddock channels, temperatures were lower and salinities and dissolved oxygen concentrations were higher than at the neighboring stations on the slope of Green Bank (station 3) and on the slope of Whale Bank (station 5). Conversely, the higher temperatures at station 7 indicate an intrusion of slope water onto the bank. Throughout the region, vertical mixing from the storms of late winter and early spring resulted in temperatures and salinities that were almost uniform, concentrations of dissolved oxygen that exceeded the saturation value, and densities that were almost invariant (σ_t = 26.0 ± 0.5) throughout the upper 50–60 m at each station. Below this homogeneous layer, density over the banks increased to the bottom because of the increasing salinity and decreasing temperature, and there was a slight decrease in density in the east to west direction across the banks.

At the South Tempest grid (Fig. 3), temperatures throughout the water column were below 0°C except at the bottom. A temperature minimum layer with values as low as −1.32°C was present at depths of 80–120 m. Dissolved oxygen concentrations were 7.5–8.2 mL/L within the layer, >8 mL/L above, and <7 mL/L below. The temperature minimum layer presumably was a remnant of the previous winter's cooling,

while the water above this was Labrador Current water, which had been modified by meltwater and slight seasonal warming, and that below was relatively unmodified Labrador Current water. At the Hibernia grid (Fig. 4), which was farther from the edge of the continental shelf and where water depths were considerably less, the "unmodified" Labrador Current water was less prominent than at the South Tempest grid. The general temperature level was appreciably higher because of the greater seasonal warming at the lower latitude, and temperatures increased in the north to south and east to west directions. Negative temperatures were present near the bottom on the two northern lines but, except for station 25, not on the two southern lines. The properties of the deeper water in this area were very similar to those at the same depths at the South Tempest grid, although there was no indication of a temperature minimum layer. Since the salinity was generally lower than at the same depths on the South Tempest grid, the amount of meltwater present was somewhat greater. In both areas, the upper 50 m was homogeneously mixed by the stormy conditions that prevailed at the time.

Volatile Hydrocarbons

Water column — Although the analytical procedure used in this study readily detected volatile hydrocarbons at concentrations of 0.02 nmol/L (0.5 ppb), methane was the only volatile hydrocarbon found in all but a very few of the 234 water samples from the Grand Banks area. While ethane, propane, and higher molecular weight volatile hydrocarbons were occasionally detected, their concentrations were never more than a few percent of that of methane. This relationship between methane and the higher homologs suggests that the methane was predominantly of recent biological origin rather than being derived from natural seepage or other escape of volatile hydrocarbons from the seabed.

Concentrations of methane in the water column of the region studied ranged from 0.41 to 1.80 nmol/L with the vast majority of the values in the 0.45−0.90 nmol/L range.[2] Such highly skewed data sets are best analyzed by lognormal statistics, although in this case the transformed data did not pass the χ^2-test for goodness of fit at the 95% confidence level (Table 1) because of the stringent requirements imposed on the test by the large number of observations. Since these conditions would have been satisfied at a somewhat lower level of confidence, the geometric mean of 0.74 nmol/L was considered to be an appropriate measure of central tendency for the overall data set and thereby provided a good estimate of the general background level for the region as a whole. When sorted geographically, the logtransformed data for the Southern Banks, Hibernia grid, and South Tempest grid passed the χ^2-test at the 95% confidence level and therefore the geometric means were the appropriate measures of central tendency for these subsets. Thus, the background levels for these areas were 0.70, 0.69, and 0.85 nmol/L, respectively. Although there were too few data to establish the distributions for the Flemish Pass and Laurentian Channel, it is likely that these data also were lognormally distributed and therefore the geometric means of 0.89 and 0.74 nmol/L provide acceptable estimates for the background levels for these areas. Student *t*-tests indicated that the background levels at the South Tempest grid and in the Flemish Pass were significantly higher (95% confidence level) than those at the Hibernia grid

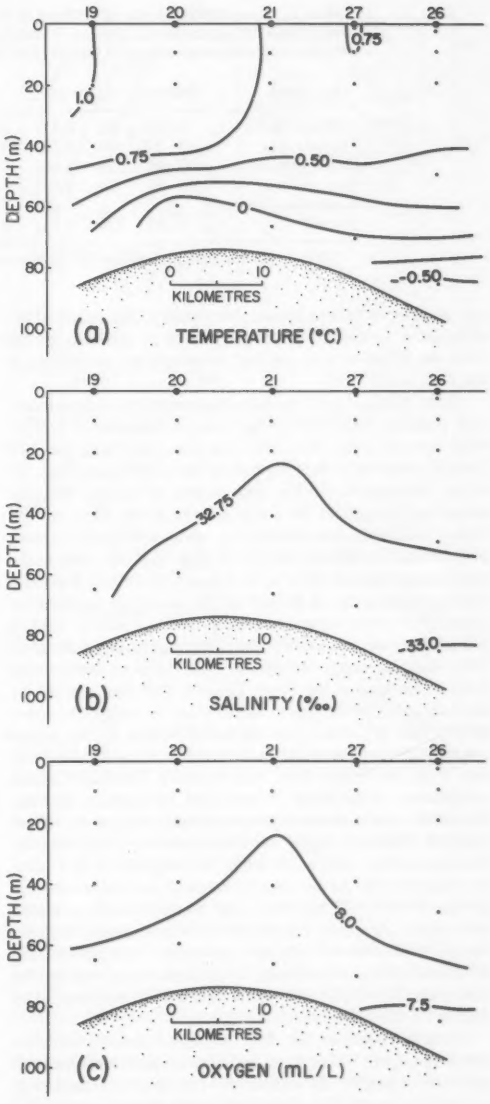

FIG. 4. Representative cross-sections showing (a) temperature, (b) salinity, and (c) dissolved oxygen data for Hibernia grid.

[2]Methane concentrations are relative to National Bureau of Standards Standard Reference Material 1658a, Methane in Air (FF 12083) 0.970 ± 0.10 μmol CH_4/mol.

TABLE 1. Concentration levels of methane in the Grand Banks area, April 7–17, 1981 (C = methane concentration in nanomoles per litre, SD = standard deviation, GM = geometric mean).

Area	Stations	n	$-\log C$	SD	GM (nmol/L)	95% confidence limits about GM (nmol/L)	χ^2-test (95% level)[a]
Southern Banks	2–10	62	0.157	0.111	0.70	0.66–0.75	Passed
Hibernia grid	13–31	94	0.167	0.047	0.68	0.67–0.70	Passed
South Tempest grid	32–43	50	0.067	0.117	0.86	0.80–0.93	Passed
Flemish Pass	11–12	20	0.047	0.162	0.90	0.75–1.06	TFD
Laurentian Channel	1	8	0.187	0.126	0.65	0.52–0.83	TFD
Overall	1–43	234	0.137	0.109	0.73	0.72–0.76	Failed

[a]TFD = too few data to establish the statistical distribution.

and over the Southern Banks. Presumably, this reflected the differences in the biological production of methane arising from the differences in ambient oceanographic conditions in the four areas.

At the Hibernia grid, methane concentrations were remarkably uniform, with 92% of the values in the range of 0.69 ± 0.09 nmol/L (Fig. 5a). This was consistent with the uniformity observed in the temperature and salinity data (Fig. 2), all of which reflected the high degree of mixing that was occurring throughout the water column at the time. All the values exceeding this interval (i.e. up to 0.90 nmol/L) were encountered at stations 13, 14, 26, and 28 at the eastern and southeastern portion of the grid. It seems, therefore, that these higher values were a feature of the relatively unmodified Labrador Current water component that was also evident in the temperature and salinity data for this portion of the grid. This was also suggested by the higher general background level of methane at the South Tempest grid (Fig. 5b) where the Labrador Current water modified by the meltwater dominated. This hypothesis was supported further by the higher concentrations of methane at stations 8–11 on the southern line (Fig. 5c) where there was a strong Labrador Current component. At the South Tempest grid, the methane distribution in the water column was more complex than at the Hibernia grid. This was, again, consistent with the more complex character of the water as shown by the temperature and salinity data (Fig. 3). At this site the range of concentrations was greater (0.59–1.75 nmol/L), and concentrations increased with depth. A strong correlation between methane concentrations and those of silicate, phosphate, and nitrate (unpublished results) at the South Tempest grid suggested that the concentrations of all these parameters were closely linked by ambient biological processes.

Along the southern line (Fig. 5c), concentrations of methane in the upper 100 m were, for the most part, between 0.45 and 0.90 nmol/L. At stations 8–11, however, there was a patch of water that contained concentrations of 0.90–1.35 nmol/L. This was in the core of Labrador Current water noted from the salinity and temperature data, and therefore, its methane concentration was more in keeping with that at the South Tempest grid than those elsewhere on the Southern Banks and Hibernia grid. Again, it would seem that the slightly higher methane concentrations in the water over the edges of the banks were the consequence of enhanced biological processes.

The background level of volatile hydrocarbons in the water of the Grand Banks at this time was only 25% of the concentrations reported by Lamontagne et al. (1973) in the surface waters of the Norwegian Sea (2.3–3.5 nmol/L and the Greenland Sea (3.3–5.1 nmol/L) and of those reported by Scranton and Brewer (1977) in the western subtropical North Atlantic (1.5–5.7 nmol/L). This, presumably, was a reflection of low rates of biological activity on the Grand Banks during early spring when water temperatures and light levels were low.

Surficial bottom sediments — Total concentrations of volatile hydrocarbons in surficial bottom sediments collected along the southern line and on the Hibernia grid (rough sea conditions precluded sampling on the South Tempest grid) ranged from 0.05 to 0.41 mmol/L and from 0.81 to 3.2 mmol/L, respectively, that is, about three orders of magnitude higher than in the overlying water column. Sediments from the southern line varied widely in grain size and texture and, at some locations, were predominantly sand, gravel, and shell fragments which were devoid of volatile hydrocarbons. Those collected at the Hibernia grid, however, were typical of marine sediments and were much more uniform in both nature and grain size. These differences could easily account for the order of magnitude difference in the concentrations of volatile hydrocarbons between the two areas. Within the Hibernia grid the sediments were sufficiently uniform to allow meaningful comparisons of concentrations to be made, and contour plots for both the total volatile hydrocarbon and methane concentrations (Fig. 6) indicated that the highest concentrations were on the western portion of the grid. It is tempting to surmise that this might indicate underlying gas and oil, and some credence for this is provided by the presence of appreciable amounts of ethane, propane, and butane in the sediment samples (Table 2). Indeed, the ratios of the concentration of methane to the combined concentrations of ethane and propane for the sediments from the Grand Banks were well within the range of 0–10 which is commonly accepted as being indicative of gas of a petroleum-related origin as opposed to gases of recent biogenic origin which typically have $C_1/(C_2 + C_3)$ ratios of 10^3–10^5 (Bernard et al. 1977).

PETROLEUM RESIDUES

Surface slicks — Visual observations of the sea surface to determine the distribution of oil in the form of surface slicks were made throughout the cruise. While working along the

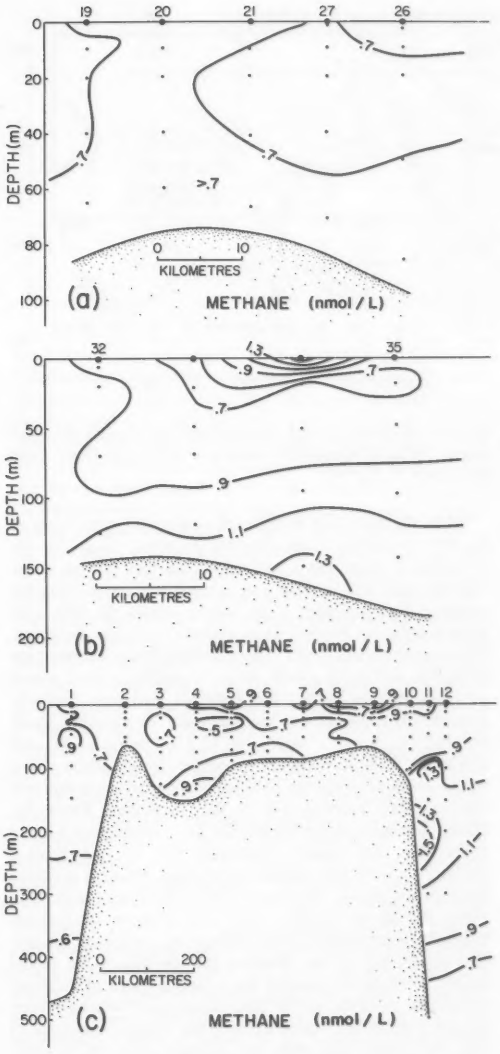

FIG. 5. Representative cross-sections showing methane concentrations at the (a) Hibernia grid, (b) South Tempest grid, and (c) southern line (April 7–17, 1981).

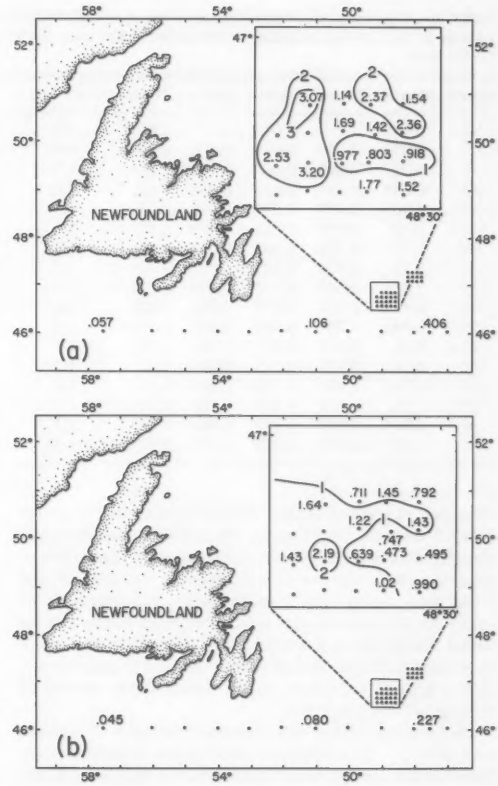

FIG. 6. Area plots showing concentrations (millimoles per litre) of (a) total volatile hydrocarbons and (b) methane in surficial sediments from the Grand Banks area (April 7–17, 1981).

southern line (stations 1–12) meteorological and oceanographic conditions ranged from ideal to favorable for the formation of surface slicks and their detection by visual means. At this time, however, none was noted. During the remainder of the cruise, while working on the Hibernia and South Tempest grids, high winds (to 30 m/s) and rough seas would have prevented the formation of slicks if oil had been present on the surface. Thus, at no time was there any indication of oil in the form of surface slicks.

Floating particulate oil — Samples for the estimation of floating particulate petroleum residues were collected at the first 27 stations after which sea conditions became too rough to deploy the sampling equipment. Floating tar concentrations ranged from 0 to 85 $\mu g/m^2$ (Fig. 7), although almost two-thirds of the samples contained no evidence of tar. Analysis of these residues by gas chromatography revealed only minor differences in the low-temperature portion of the chromatograms, and since these differences could easily have arisen from differences in the degrees of weathering, it was probable that all the residues were from a common source.

Since there were too few samples to establish the statistical distribution of the data, it was not possible to obtain an estimate of the existing background level of tar on the Grand Banks from this very limited data set alone. However, data collected between 1971 and 1974 suggested that the background level on the Grand Banks at that time was less than

TABLE 2. Concentrations (millimoles per litre) of volatile hydrocarbons in the surficial sediments of the Grand Banks area, April 7–17, 1981.

Station	Methane	Ethane	Propane	Butane	Total	$C_1/(C_2 + C_3)$
1	0.045		0.012		0.057	3.8
7	0.080	0.008	0.010	0.008	0.106	4.4
11	0.227	0.090	0.058	0.031	0.406	1.5
13	0.990	0.353	0.117	0.055	1.52	2.1
14	1.02	0.459	0.221	0.071	1.77	1.5
18	1.43	0.779	0.224	0.099	2.53	1.4
21	1.22	0.354	0.099	0.018	1.69	2.7
22	2.19	0.729	0.197	0.081	3.20	2.4
23	0.639	0.238	0.071	0.029	0.977	2.1
24	0.473	0.221	0.075	0.034	0.803	1.6
25	0.495	0.297	0.086	0.040	0.918	1.3
26	1.43	0.612	0.213	0.103	2.36	1.7
27	0.747	0.477	0.135	0.064	1.42	1.2
28	0.792	0.495	0.180	0.075	1.54	1.2
29	1.45	0.644	0.194	0.085	2.37	1.7
30	0.711	0.486	0.149	0.068	1.41	1.1
31	1.64	0.887	0.369	0.171	3.07	1.3

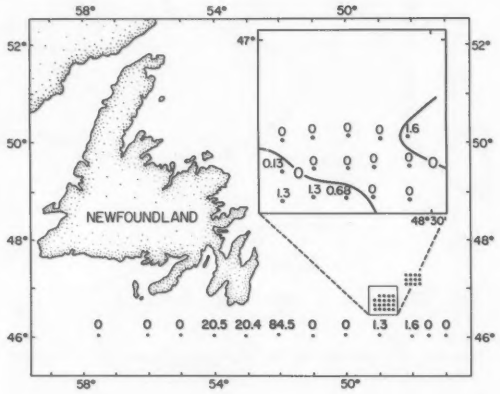

FIG. 7. Area plot showing concentrations (micrograms per square metre) of floating particulate petroleum residues in the Grand Banks area (April 7–17, 1981).

10 μg/m² (Levy and Walton 1976). Farther south in waters dominated by the Gulf Stream, tar concentrations increased abruptly whereas farther to the north tar was seldom encountered. It would seem that the tar present at stations 4, 5, and 6 had been carried there from the south, and therefore, the values for the other stations were more representative of the Grand Banks area as a whole. Thus, the southward flow of unpolluted Labrador Current water continued to maintain relatively pristine conditions on the Grand Banks insofar as floating tar was concerned.

Dissolved and Dispersed Petroleum Residues — Surface microlayer — Concentrations of dissolved/dispersed petroleum residues in the surface microlayer of the Grand Banks area during April 1981 ranged from 14 to 440 μg/L, although most of the values were in the range of 25–50 μg/L.[3] After logarithmic transformation, the requirements of the χ^2-test for goodness of fit were met at the 95% level of confidence, and therefore, the geometric mean was the appropriate measure of central tendency. Thus, the general level of contamination of the surface microlayer along the southern line and at the Hibernia grid at the time was 28.9 μg/L (95% confidence limits about the geometric mean being 20.3–41.3 μg/L) (Table 3). This was considerably higher than the level of 7.5 μg/L (95% range 5.0–11.4 μg/L) observed in Baffin Bay in 1977 (Levy 1979a) and was probably a direct consequence of the higher general level of human activity in the Grand Banks area.

[3]All concentrations of dissolved/dispersed petroleum residues are expressed in terms of Bunker C fuel oil from the tanker *Arrow*, which sank off the Nova Scotia coast in 1970. This oil has been used as the reference material throughout our studies of background levels in the waters off the east coast of Canada (Levy 1971, 1972; Levy and Walton 1973) and in the Canadian Arctic (Levy 1979a, 1981) and ensures that data from this laboratory remain internally consistent. To relate our results with those based on chrysene, the intensity of fluorescence emission at 360 nm on excitation at 310 nm of this oil is 0.221 times that of chrysene under the same conditions.

When the data were plotted and contoured on the basis of the 95% confidence limits about the geometric mean (Fig. 8), it became evident that a "polluted" area was present at the Hibernia grid and possibly also at stations 1 and 6 along the southern line. Although a few values outside the 95% confidence range for the data set as a whole were to be expected, there was much less than 1 chance in 1000 that a concentration as high as 440 μg/L would occur. Therefore, a local source of contamination within the Hibernia grid was probably present. Since this site was less than 6 km "downstream" from the drill rig *Ocean Ranger*, (46°47.3′N, 48°47.17′W) and within the zone occupied by its supply vessels, there was a strong implication that the elevated concentrations in this area were a direct consequence of their activities. From this source, the observed distribution of the contaminated surface microlayer was readily accounted for by the south–southwesterly flow of surface water. Thus, the data indicated that the oil industry, even at the level of its operations in April 1981, was already having a detectable effect on the concentration of dissolved/dispersed petroleum residues in the surface microlayer on the Hibernia grid portion of the Grand Banks. It might be expected that a similar patch of localized contamination of the surface microlayer would also have been present at the South Tempest grid in the vicinity of stations 33 and 34 where the drill rig *Zepata Lfae* (47°07.2′N, 47°57.3′W) and its support vessels were operating. However, when this area was surveyed, wind (18–30 m/s) and sea conditions precluded sampling the surface microlayer. Indeed, under such conditions, the surface microlayer can scarcely be considered to exist. It should be appreciated also that enrichment of the sea surface by hydrophobic substances is highly dependent on ambient conditions, and therefore, the concentrations of these substances at the sea surface may be highly variable in both time and space.

Water column — Concentrations of dissolved/dispersed petroleum residues in the water column of the Grand Banks area in April 1981 ranged from 0.05 (detection limit of the

TABLE 3. Concentration levels of dissolved/dispersed petroleum residues in the Grand Banks area, April 7–17, 1981 (C = concentration in micrograms per litre, SD = standard deviation, GM = geometric mean).

Area	Stations	n	$\overline{\log C}$	SD	GM (μg/L)	95% confidence limits about GM (μg/L)	χ^2-test (95% level)[a]
Southern Banks	2–10	61	−0.640	0.348	0.23	0.19– 0.29	Passed
Hibernia grid	13–31	92	−0.796	0.313	0.15	0.19– 0.14	Failed (barely)
South Tempest grid	32–43	51	−0.872	0.289	0.13	0.16– 0.11	Passed
Flemish Pass	11–12	20	−0.697	0.312	0.20	0.14– 0.28	TFD
Laurentian Channel	1	10	−0.201	0.352	0.63	0.35– 1.1	TFD
Overall	1–43	234	−0.738	0.347	0.18	0.17– 0.20	Failed
Surface microlayer	1–43	25	1.461	0.367	28.9	20.3 –41.3	Passed

[a]TFD = too few data to establish the statistical distribution.

method 0.01) to 4.05 μg/L. As is usually the case with data for dissolved/dispersed petroleum residues, the data set was highly skewed, with most of the values near the lower end of the range and only a very few at the higher end (only 10 of the 234 values exceeded 1 μg/L). Most of these higher values were encountered along the southern line and most, but not all, were in the upper 20 m. Such data are best analyzed by lognormal methods, and since the logtransformed data for the Southern Banks and South Tempest grid passed the χ^2-test at the 95% level of confidence and those for the Hibernia grid almost passed, the geometric means provided the best measures for the background levels in these areas (Table 3). The data suggested that the concentration level on the Southern Banks was somewhat higher than those at the Hibernia and South Tempest grids. Although t-tests indicated that the differences in the concentration levels in these areas were statistically significant, they are of little or no significance in terms of assessing environmental quality. Therefore, the data can be considered to be representative of the area as a whole without regard for these small geographical differences.

Although the overall data set after transformation failed to meet the stringent requirements imposed on the χ^2-test at the 95% confidence level by the large number of values, the distribution was sufficiently close to lognormal to be best analyzed by lognormal methods. On this basis, the geometric mean of the overall data set, 0.18 μg/L (95% interval about the mean, 0.17–0.20 μg/L), provided a good estimate of the background level in the water column of the Grand Banks area during April 1981. This is the lowest level found so far in the waters of any region of eastern Canada; for example, previous work has shown that the general background level was approximately 2 μg/L in waters of the Scotian Shelf and Gulf of St. Lawrence (Levy 1971, 1972, unpublished data; Levy and Walton 1973), 0.86 μg/L in the Labrador Sea (unpublished data), and 0.48 μg/L in Baffin Bay away from the influence of natural seepage on the continental shelf (Levy 1979a). It is noteworthy that the background levels for the more remote northern areas were markedly lower than those for the Scotian Shelf and Gulf of St. Lawrence, and this, presumably, was a reflection of the differences in the nature and magnitude of the inputs to the various areas. For example, the major input to the remote areas is currently thought to be fallout from the atmosphere of polynuclear aromatic hydrocarbons derived from the high-temperature combustion of

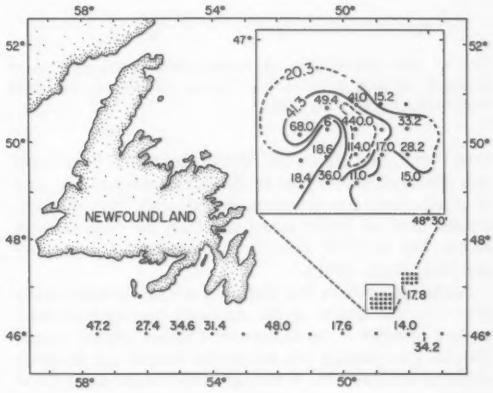

FIG. 8. Area plot showing concentrations (micrograms per litre) of dissolved/dispersed petroleum residues in the sea surface microlayer in the Grand Banks area, (April 7–17, 1981).

organic materials (Levy and Ehrhardt 1981). In the more accessible areas, direct inputs of oily substances from shipping and other human activities are superimposed on the background from fallout. Further, atmospheric fallout is a diffuse source and results in a very uniform level over large geographic areas, whereas the more localized sources such as discharges from ships, etc., not only contribute to a higher general background level but also give rise to greater variability in the data and to the existence of concentration "anomalies." The data collected during this survey suggested that the existing background level of dissolved/dispersed petroleum residues in the waters of the Grand Banks was derived primarily from diffuse sources, and therefore, any impact of the oil industry's activities on the concentrations of dissolved/dispersed petroleum residues in the water column of the Grand Banks at the time of this study could not be detected above the existing background level derived from other sources.

Surficial bottom sediments — Concentrations of petroleum residues in the surficial bottom sediments ranged from 0 to 5.5 μg/g of freeze-dried sediment along the southern line and

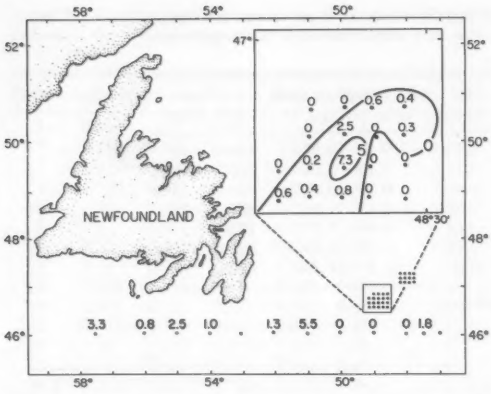

FIG. 9. Area plot showing concentrations (micrograms per gram) of petroleum residues in the surficial bottom sediments of the Grand Banks area (April 7–17, 1981).

from 0 to 7.25 μg/g on the Hibernia grid (Fig. 9). (Rough seas prevented sampling on the South Tempest grid.) By way of comparison, concentrations in sediments from the continental shelf of Baffin Island and from the deep areas of Baffin Bay in 1978 were 0–2.5 and 0–7.5 μg/g, respectively (Levy 1981).

Along the southern line there was a wide variation in the grain size and texture of the sediments ranging from fine-grained material in the Laurentian Channel (station 1) and Flemish Pass (station 12) and in the Halibut and Haddock channels (stations 3 and 4) through sand (stations 8 and 10) to a sediment that was predominantly shell fragments (station 7) and coarse gravel (station 5) on the banks. Since the amount of organic substances in marine sediments is dependent on the grain size and nature of the sediments, a comparison of the concentrations of petroleum residues along this line was not possible. It is noteworthy, however, that the highest concentration of petroleum residues, 5.5 μg/g, was present in a sample composed almost entirely of shell fragments (station 7). The sandy samples (stations 8, 9, and 10) contained no evidence of oil.

At the Hibernia grid, sediment grain sizes and textures varied less widely and a comparison of petroleum residue concentrations was meaningful. The highest concentrations in this area were found at stations 23 and 21 where the sediment was a mixture of sand and shell fragments. Concentrations diminished outwards from this area, and in the northwest and southwest portions of the grid, petroleum residues were not detected. Since *Ocean Ranger* was operating just north of station 21 and the prevailing current was southwestward, there was a strong implication that the sediments in this area were receiving oily substances from the industry's activity.

Concluding Remarks

The results of this study demonstrated that the background level of petroleum-related substances, both the low molecular weight volatile hydrocarbons and the higher molecular weight aliphatic and aromatic hydrocarbons, in the waters and surficial sediments of the Grand Banks area in 1981 were among the lowest found anywhere in eastern Canada including remote regions of the Arctic. However, the results also provided evidence that the petroleum industry was already having a detectable impact, albeit small, on the existing low background levels of petroleum residues in the surface microlayer and bottom sediments of the area. Although this is, as yet, no cause for environmental alarm, it is a portent of what can be expected in the future. In view of the existing pristine nature of the area, continued exploration and eventual production, even in the absence of the inevitable mishap, can only lead to future increases in the level of contamination in this area. This poses no small challenge to the industry if it is to carry out its operations in such a manner that the environment is not degraded to the extent that the fishery is eventually jeopardized. It also demonstrates the need for a monitoring program to provide an early alert when levels of contamination approach the point where environmental damage might begin to occur so that the appropriate measures can be taken to avert permanent damage.

Acknowledgments

I would like to thank the officers and crew of CSS *Dawson* for their cooperation and support during this cruise; to them goes the credit for a successful cruise under difficult conditions. Similarly, the efforts of the scientific and technical personnel, both aboard ship and in the laboratory, are gratefully acknowledged.

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Particulate Hydrocarbon and Coprostanol Concentrations in Shelf Waters Adjacent to Chesapeake Bay[1]

T. L. WADE, G. F. OERTEL, AND R. C. BROWN[2]

Department of Oceanography, Old Dominion University, Norfolk, VA 23508, USA

WADE, T. L., G. F. OERTEL, AND R. C. BROWN. 1983. Particulate hydrocarbon and coprostanol concentrations in shelf waters adjacent to Chesapeake Bay. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 34–40.

Adjacent to the entrances of major estuaries, the concentrations and distributions of particulate coprostanol, hydrocarbons, and total suspended matter are controlled by both small-scale and large-scale processes. These processes result in the development of spatially separate plumes of coprostanol, hydrocarbons, and total suspended matter. Particle buoyancy appears to be a major factor controlling the sorting of particles into the three discrete plumes. At the inner shelf adjacent to the Chesapeake Bay entrance, patchiness of coprostanol, hydrocarbon, and total suspended matter concentrations is also controlled by alongshore wind stress which enhances the uncoupling of the distal ends of plumes. While Chesapeake Bay appears to be a chronic source of anthropogenic materials to adjacent shelf water, major pathways of several pollutants (sewage derived and hydrocarbons) do not spatially coincide with turbid or low-salinity plumes.

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Près de l'entrée d'estuaires d'importance, les concentrations et distributions du coprostanol particulaire, des hydrocarbures et de la matière en suspension totale sont réglées par des processus tant à petite qu'à grande échelle. Ces processus sont responsables de la formation de panaches spatialement distincts de coprostanol, d'hydrocarbures et de matière en suspension totale. La flottabilité des particules semble être un facteur majeur de régulation du triage des particules dans trois panaches distincts. Sur le plateau intérieur du voisinage de l'entrée de la baie de Chesapeake, la répartition irrégulière de la concentration du coprostanol, des hydrocarbures et de la matière en suspension totale est également réglée par la poussée du vent le long du rivage, qui favorise la séparation des extrémités distales des panaches. Alors que la baie de Chesapeake semble une source persistante de matériaux anthropogènes pour les eaux avoisinantes adjacentes au plateau, les voies principales de plusieurs polluants (dérivés d'égouts et hydrocarbures) ne coïncident pas spatialement avec les panaches turbides ou de faibles salinités.

Received March 18, 1982
Accepted November 25, 1982

Reçu le 18 mars 1982
Accepté le 25 novembre 1982

PETROLEUM hydrocarbons are entering the marine environment at a rate of approximately 6×10^6 t annually (National Academy of Sciences (NAS) 1975). Highly publicized inputs from direct spills, drilling, shipping, and refinery operations account for only 40% of the total petroleum hydrocarbon input. Chronic inputs, which have not been extensively studied, account for the remaining 60% of the petroleum hydrocarbon input. A significant portion of these chronic inputs may impact coastal environments (NAS 1975).

Van Vleet and Quinn (1977) estimated that 0.2×10^6 t of petroleum hydrocarbons may be transported annually to the marine environment from municipal treatment plants. Approximately 95% of this input is associated with suspended materials, and about half of this is removed to the sediments in the vicinity of the discharge (Van Vleet and Quinn 1978).

Coprostanol (5β-cholestan-3β-ol) is a unique biochemical tracer that is formed exclusively by enteric bacterial reduction of cholesterol in man and certain animals (Rosenfield et al. 1954; Rosenfield and Gallagher 1964; Teshima and Kanazawa 1978; Murtaugh and Bunch 1967). The detection of coprostanol in marine samples indicates fecal contamination from either domestic waste or runoff from pastures and barnyards (Murtaugh and Bunch 1967). When municipal treatment plant effluents enter the marine environment, co-

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Mote Marine Laboratory, 1600 City Island Park, Sarasota, FL 33577, USA.

Printed in Canada (J6843)
Imprimé au Canada (J6843)

prostanol associates with particles that may be deposited near the outfall or transported away from the outfall site.

Hydrocarbon concentrations are generally higher on particles less than 44 μm than they are on larger particles (Meyers and Quinn 1973; Wade and Quinn 1979). The adsorption of hydrocarbons to very fine grained particulate materials favors dispersal over sedimentation.

The objectives of this study were to determine if particulate hydrocarbons and fecal contaminants are exported from large estuaries to the adjacent shelf waters and to describe the physicochemical processes influencing their collection and dispersion. Chesapeake Bay, one of the largest estuaries in the world, provided a good prototype for this study.

Materials and Methods

One hundred and fifty-four water samples were collected during cruises aboard NOAA ships *Delaware II* (June 17–23, 1980) and *Kelez* (June 24–27, 1980; October 14–22, 1980), and Old Dominion University's research vessel, *R/V Linwood Holton* (June 19–24, 1980). Sample stations were located adjacent to the entrance of Chesapeake Bay (e.g. see Fig. 1). Water samples were collected near the surface, at intermediate depths, and near the bottom. Collection was made with a clean metal bucket or a 20-L Niskin bottle. The first samples taken from the collection containers were for total suspended matter (TSM) analyses. Then, the sample vessel for hydrocarbon and coprostanol analyses (a 20-L metal can or glass carboy) was rinsed with sample water, and the entire contents of the Niskin bottle were drained into the sample vessel by removal of the bottom stopper of the Niskin bottle.

The water samples for TSM and hydrocarbon/coprostanol analyses were filtered through preignited Gelman A/E glass fiber filters as soon after collection as possible (within 2 h). The filters containing the subsamples for TSM analyses were refrigerated, whereas filters containing subsamples for hydrocarbon/coprostanol analyses were frozen during the temporary storage before transport to the laboratory.

Details of the analytical procedures have been described for TSM (Manheim et al. 1970), hydrocarbons (Wade and Quinn 1975), and coprostanol (Hatcher and McGillivary 1979). The hydrocarbon/coprostanol analyses entailed placing the filter with its associated retained material in a round-bottom flask. Internal standards of docosane, hexaethylbenzene, and nonadecanol were added and the sample saponified/extracted under reflux for 2 h. The extract was filtered and the filtrate was partitioned against 100 mL of 10% NaCl solution, acidified to a final pH of 2 or less with HCl. The aqueous phase was extracted a total of three times using 50 mL of dichloromethane each time. The combined dichloromethane extracts were taken to dryness on a rotary flash evaporator. The residue was dissolved in hexane and placed on an alumina–silica gel column. The hydrocarbon fraction was eluted with 10 mL of hexane; then, 10 mL of methanol was used to remove the sterol fraction.

These fractions were analyzed on a Hewlett-Packard 5830 gas chromatograph, equipped with a 25-m fused silica WCOT capillary column coated with either methysilicone or SE-54. The analyses were done by temperature programming from 80 or 150°C to 270 or 300°C at 8 or 10°·min^{-1}. The eluting materials were detected with a flame ionization detector. The detector response was recorded and integrated with a Hewlett-Packard model 18850A reporting integrator. The concentration of coprostanol was calculated by comparison of integrator counts of coprostanol and the internal standard, nonadecanol. The areas of resolved hydrocarbon and unresolved complex hydrocarbon mixtures were determined by planimetry. Comparison of areas of the resolved peaks and unresolved complex mixtures, with the area of internal standard(s) (docosane and/or hexaethylbenzene), allows the concentration of hydrocarbons to be calculated.

Procedural blanks were processed onboard ship and analyzed in the same manner as all samples. Blanks contained no detectable unresolved complex mixtures of hydrocarbons and

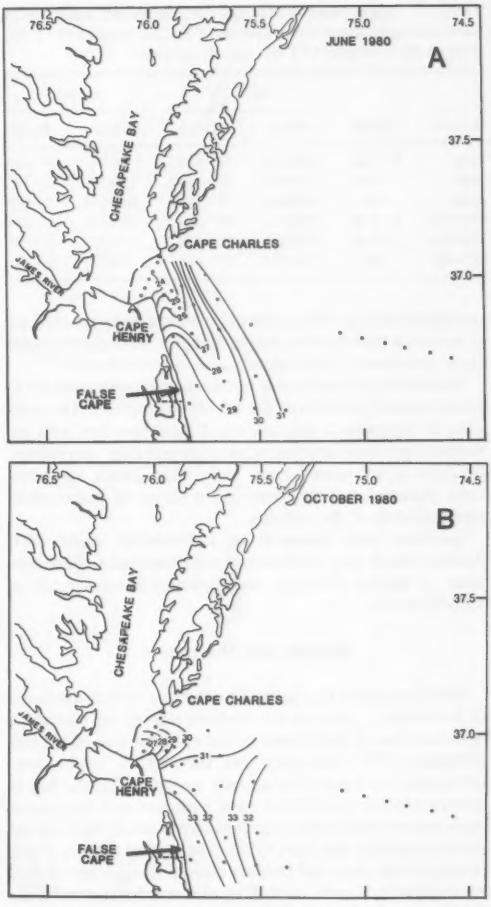

FIG. 1. Surface salinity (‰) distribution for (A) June 1980 and (B) October 1980. Sampling stations indicated by dots.

TABLE 1. Means (number of samples in parentheses) and ranges of particulate coprostanol concentrations of surface samples (0–1 m), below-surface samples (>1 m), and all samples.

		ng·L^{-1}		ng·mg^{-1}	
Cruise	Depth	Mean	Range	Mean	Range
June	0–1 m	198(28)	72–1042	84(27)	5–315
June	>1 m	279(38)	77–1014	115(38)	5–399
June	All	244(66)	72–1042	102(65)	5–399
October	0–1 m	163(17)	47–394	54(14)	5–153
October	>1 m	207(40)	41–438	53(33)	8–201
October	All	194(57)	41–438	53(47)	5–201

no coprostanol; however, they did contain a maximum of 7 μg of resolved hydrocarbon peaks. Samples were corrected for these procedural blank values.

Standard hydrocarbon and sterol mixtures were analyzed to insure proper operation of the gas chromatograph. The presence of coprostanol was confirmed by coinjection with authentic coprostanol and formation of trimethysilyl derivatives. Analyses of the various ships' fuels, bilge waters, and lubricants indicated that they were not a source of hydrocarbon contamination of the samples.

Salinities were measured on a Guideline model 8400 Autosal which was standardized with standard Copenhagen water of known chlorinity and assuming a salinity (S) of 1.80655‰·Cl.

Results and Discussion

The Chesapeake Bay generally exhibits a surface discharge of low-salinity water on the southern side of the bay and a bottom influx of shelf water on the northern side of the bay (Pritchard 1962; Beardsley and Hart 1978). Under low-turbulence conditions, low-salinity water leaving the bay is deflected to the right by the earth's rotation and the general circulation of shelf waters and therefore normally flows to the south (Beardsley and Hart 1978). The surface salinity distributions for the June and October cruises illustrate two different trajectories for the outwelling of low-salinity water from the Chesapeake Bay (Fig. 1). The June pattern exhibited the anticipated southerly flow of low-salinity water (24–31‰) from the bay. During October, the low-salinity water (27–31‰) extended in an east-northeast direction away from the bay entrance. In October, relatively high salinities in the bay entrance were probably due to the severe drought experienced in the Chesapeake Bay drainage basin during the latter months of 1980.

Wind stress also may be an important factor affecting the diversion of the outwelling bay water mass and the resultant salinity distribution. The resultant wind stress and direction in June (18 d, beginning 7 d prior to the experiment) and in October (16 d, beginning 7 d prior to the experiment) were 0.79 g·cm^{-1}·s^{-2} west–northwest (291°) and 2.09 g·cm^{-1}·s^{-2} east–northeast (63°), respectively. In shallow areas, surface water has been observed to flow in the same direction as the wind stress (Duxbury 1971). Wind stress during this study would tend to divert the ambient

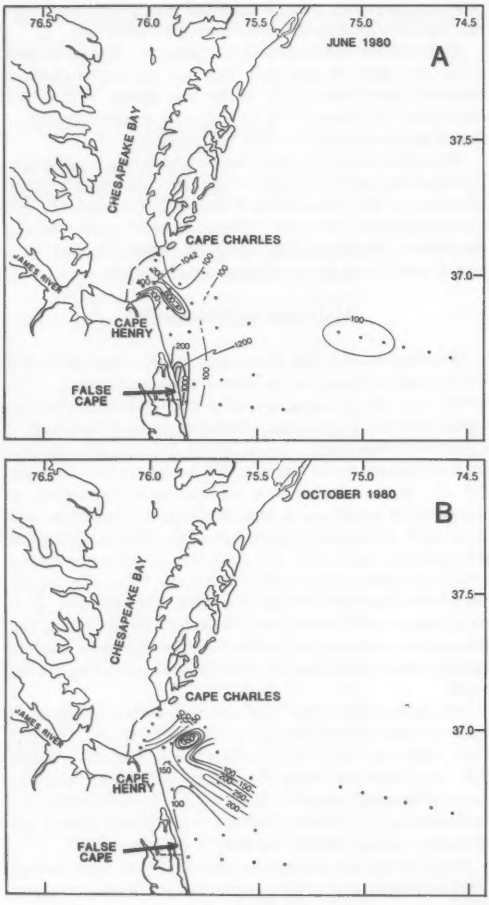

FIG. 2. Surface particulate coprostanol concentration (nanograms per litre) for (A) June 1980 and (B) October 1980.

TABLE 2. Means (number of samples in parentheses) and ranges of particulate hydrocarbon concentrations of surface samples (0–1 m), below-surface samples (>1 m), and all samples.

		g·L^{-1}		mg·g^{-1}	
Cruise	Depth	Mean	Range	Mean	Range
June	0–1 m	6.6(42)	<1–31.6	3.0(41)	<1–13.8
June	>1 m	4.6(52)	<1–28.1	1.7(52)	<1–9.5
June	All	5.5(94)	<1–31.6	2.3(93)	<1–13.8
October	0–1 m	1.3(16)	<1–4.8	0.6(14)	<1–3.0
October	>1 m	3.6(44)	<1–14.4	1.2(36)	<1–7.1
October	All	3.0(60)	<1–14.4	1.0(50)	<1–7.1

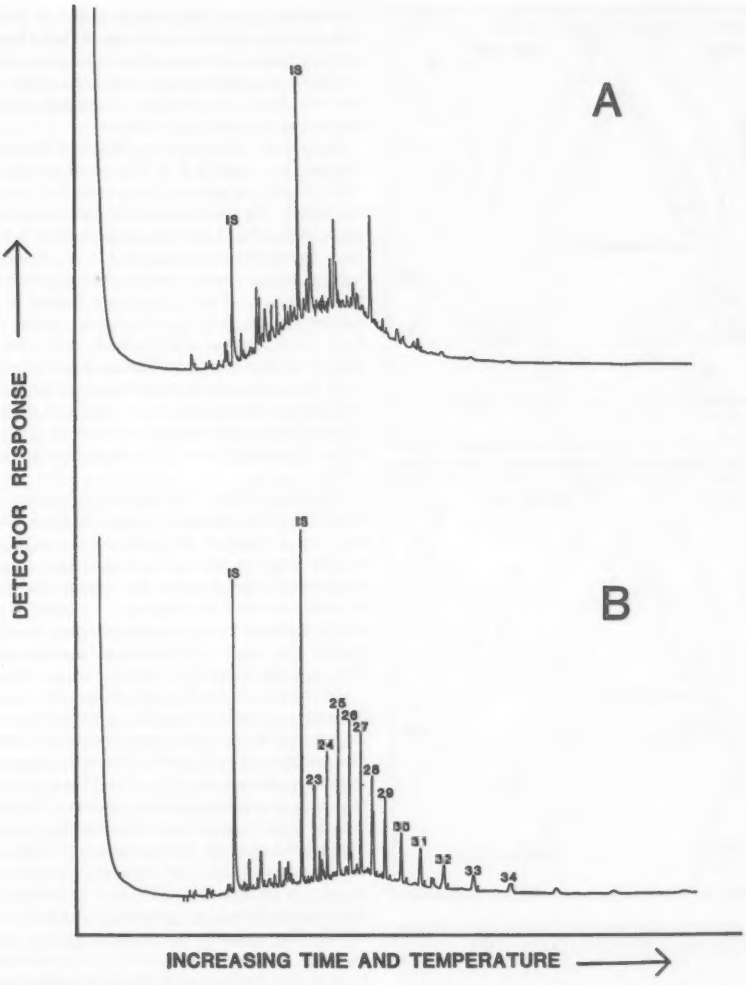

FIG. 3. Gas chromatograms of two types of particulate hydrocarbon distributions. IS, internal standards; 23–34, *n*-alkanes.

surface water flow in a west–northwest direction in June and in an east–northeast direction in October. However, the actual water movement is the resultant of the interaction between tidal, baroclinic, and barotrophic flows, as well as wind stress and freshwater inputs.

Coprostanol concentrations adjacent to the Chesapeake Bay entrance ranged from 41 to 1042 $ng \cdot L^{-1}$. These concentrations are similar to previously reported coprostanol concentrations for the Clyde Estuary, Scotland (Goodfellow et al. 1977), the Ariake Sea, Japan (Kanazawa and Teshima 1978), and Tokyo Bay, Japan (Ogura 1972). The reporting of "relative" coprostanol concentrations (Hatcher and McGillivary 1979) is not justified for these studies or the current study because the effects of dilution, with large amounts of coarse grain materials, are not relevant for water samples. The mean surface coprostanol concentration for all samples is lower than the mean concentration at depths below 3 m (Table 1). This increased concentration with depth may be caused by the settling of sewage-associated particles as they leave the bay and/or the resuspension of contaminated sediments. A decrease in the mean coprostanol concentration between June and October 1980 may be related to differences in discharge

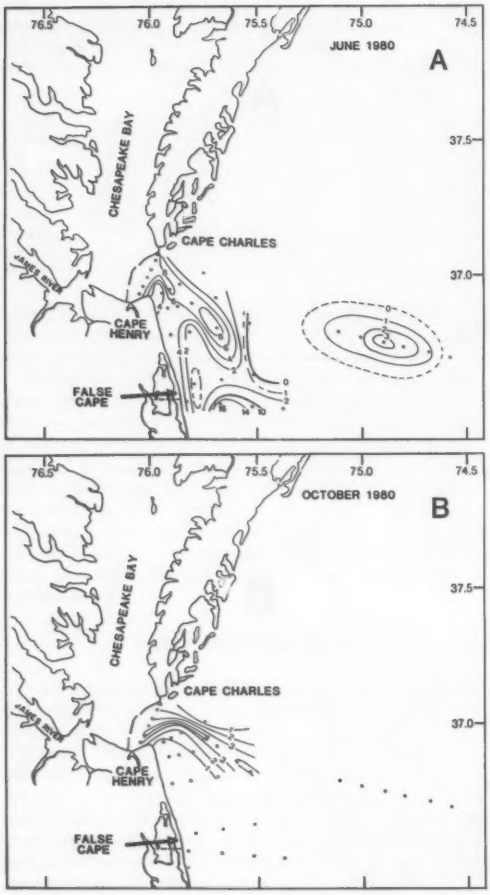

FIG. 4. Surface particulate hydrocarbon concentrations (micrograms per litre) for (A) June 1980 and (B) October 1980.

from Chesapeake Bay during these months. The stream flow into the bay in June was approximately 1250 $m^3 \cdot s^{-1}$, whereas in October it was only approximately 250 $m^3 \cdot s^{-1}$ (Ruzecki 1981). The coprostanol concentrations are also reported in nanograms of coprostanol per milligram of TSM (Table 1). No apparent correlation was found between the concentrations of TSM and coprostanol. The range of concentrations, however, are similar to coprostanol concentrations found in seabed materials near sewage outfalls in lower Chesapeake Bay (R. C. Brown, unpublished data).

Surface coprostanol concentrations (Fig. 2) are spatially similar to the surface salinity distribution (Fig. 1). In June 1980, relatively high coprostanol concentrations extended in a southerly direction from the bay mouth. In October, a relatively high coprostanol concentration (>100 $ng \cdot L^{-1}$) formed a bifurcated plume that extended offshore from Cape Henry, VA; one fork extended to the east of Cape Henry and the other to the southeast. Isolated areas of relatively high coprostanol concentration offshore and near False Cape, VA, may have resulted from resuspension of contaminated sediments or patches of outwelled bay water.

Particulate hydrocarbons (PHC) at the Chesapeake Bay entrance were detected in 75% of all samples and in 88 and 53% of the samples collected in June and October, respectively. All samples contained an unresolved envelope of peaks indicative of anthropogenic or fossil hydrocarbon materials (Farrington and Meyers 1975). The hydrocarbon concentrations ranged from below the detection limit of <1 $\mu g \cdot L^{-1}$ to 32 $\mu g \cdot L^{-1}$ (Table 2) and are similar to concentrations reported in the literature for coastal waters (Zsolnay 1971; Levy 1971; Gordon and Michalik 1971). The PHC concentrations (Table 2) on a milligram of hydrocarbon per gram of TSM basis were within the range of concentrations for seabed sediments collected from highly polluted estuarine areas with chronic hydrocarbon inputs or where oil spills have occurred (Van Vleet and Quinn 1978; Keizer et al. 1978; Teal et al. 1978).

The mean surface PHC concentration was higher than the mean PHC concentration at depth in June, while the reverse was true in October. The higher mean surface concentration in June may be the result of the larger number of surface samples collected near the bay entrance in June. In October, a greater number of samples were taken in offshore areas where settlement and resuspension may have been more important. The samples collected in June also had higher mean PHC concentrations than the October samples.

The hydrocarbons from this study area show two distinctly different gas chromatographic patterns (Fig. 3). One type of chromatogram consists almost entirely of an unresolved complex mixture of peaks with few resolved peaks and no detectable *n*-alkane peaks (Fig. 3A). This type of chromatogram is similar to chromatographic patterns of hydrocarbon distributions found in estuarine sediments (Wade and Quinn 1979). The second type of chromatogram contains an unresolved complex mixture of peaks, as well as resolved peaks of $n\text{-}C_{23}$ to $n\text{-}C_{34}$ *n*-alkanes (Fig. 3B). This is similar to hydrocarbon distributions found for some pelagic tar particles (Wade et al. 1976). The majority of chromatograms were similar to Fig. 3A, which is characteristic of weathered oil that has been in the marine environment for more than a few days (NAS 1975).

The distributions of PHC concentrations for June and October are dramatically different (Fig. 4). June PHC concentrations were generally higher than October PHC concentrations and illustrated an area of relatively high concentrations extending in a southwest direction from the bay mouth. This plumate area of relatively high PHC concentration was seaward of the axis of the outwelling, low-salinity bay water (Fig. 1) and may be related to the interface between shelf and bay waters (S = 30–31‰). In October, a plumate area of relatively high PHC concentrations extended in an offshore direction. As was the case in June, the PHC plume in October appeared to be located along the interface between shelf and bay waters rather than along the axis of the low-salinity outwelling. It appears that PHC preferably collected

along the 30−31‰ isohaline. This isohaline corresponds approximately to the interface between shelf and bay waters. Plume fronts associated with this region may have an important effect on PHC concentrations (Klemas and Polis 1977; Oertel and Dunstan 1981; Garvine and Monk 1974).

The concentration of TSM in the outwelling water mass from the bay entrance is decreased by turbulent mixing with "clearer" shelf water (dilution) and by sedimentation of particles. TSM concentrations may be increased locally by resuspension of sediment from the seabed caused by currents or waves. During the 1980 experiments, the concentration of TSM generally decreased with distance away from the bay entrance (Fig. 5). In June 1980, relatively high concentrations ($2-3$ mg·L^{-1}) of TSM extended from the bay entrance to False Cape, VA, in a narrow zone along the coast. This zone was landward of the axis of low-salinity water leaving the bay. Adjacent to Cape Henry, VA, a relatively high TSM ($2-3$ mg·L^{-1}) concentration extended northeastward approximately 2−3 nautical miles. In October 1980, relatively high TSM concentrations ($2-6$ mg·L^{-1}) extended approximately due east from the bay entrance. The axis of this plumate area of high TSM concentration was approximately coincident with the axis of a relatively low-salinity plume. The concentration of suspended matter in the receiving shelf water was generally less than 1 mg·L^{-1}. Sixty to eighty percent of the particulate matter in the "turbid plume" was composed of inorganic matter, i.e. estimated to have had a density similar to quartz (2.65 g·cm^{-3}).

The results of these studies at the Chesapeake Bay entrance illustrate that the transport of coprostanol, PHC, and TSM from large estuaries to the inner shelf may follow significantly different pathways. At the Chesapeake Bay entrance, the spatial distribution of these nonconservative characteristics (coprostanol, PHC, and TSM concentration) of the water illustrated three irregular but distinct plumate areas. The PHC plume did not coincide with the low-salinity plumes but appeared to be associated with the boundaries between the low-salinity plumes and receiving shelf water. Since these boundaries are often characterized by convergent surface flows (Oertel and Wade 1981), it is postulated that buoyant materials, including PHC, collect in these regions and that estuarine and plume fronts function as major collectors and pathways for the seaward dispersion of PHC and other buoyant materials.

TSM plumes coincided with coastal boundaries and the proximal areas of the low-salinity plume. Resuspension from seabed shear is the major process contributing to TSM enrichment along coastal boundaries. As waves and strong currents exert a stress on the seabed, sediments are elevated into the water column in a turbulent flow. Dispersion of these particles was affected by a northward flowing coastal current impinging on False Cape, VA. Although this area is adjacent to the bay entrance it was not spatially coincident with the axis of the low-salinity plume. TSM plumes associated with relatively low salinities were apparently entrained in the hypopycnal flow associated with a buoyant surface plume. However, much of the suspended matter "settles out" in the inner portion of the low-salinity plume due to the large negative buoyancy and high settling rates of most particles.

The contrasting buoyant characteristics of coprostanol, PHC, and TSM produced a spatial separation of their respective plumes. The PHC and TSM plumes are separate from the outwelling of low-salinity water, while the coprostanol distribution appears to be weakly associated with the low-salinity plume of the Chesapeake Bay. Coprostanol that is associated with particles or aggregates of particles that are approximately neutrally buoyant is entrained with the moving water mass. At the Chesapeake Bay entrance, relatively high concentrations of coprostanol define two main zones of water movement with associated coprostanol sources. The east−west trend defines the low-salinity plume of the Chesapeake Bay. The relatively high concentration of coprostanol associated with False Cape, VA, may be associated with a north-flowing coastal current that is resuspending coprostanol-rich sediments near False Cape, VA.

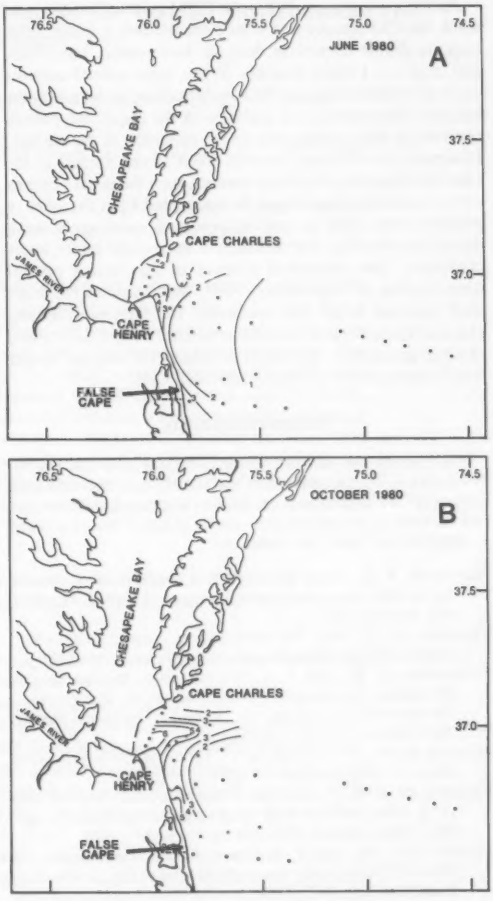

FIG. 5. Surface total suspended material concentrations (milligrams per litre) for (A) June 1980 and (B) October 1980.

As the coprostanol, PHC, and TSM plumes expand seaward, the Chesapeake Bay inlet currents have a lesser influence on plume dispersion than the barotrophic, baroclinic, and local wind stress currents. When these coastal currents exert an onshore force on the bay outwelling water mass, the buoyant characteristics of particles in the respective plumes continue to play a major role in the evolution of the plumes. However, when coastal currents exert forces normal to the trend of outwelling bay water masses, then the distal portions of the respective plumes may be uncoupled from the inner or proximal ends. This uncoupling process is most apt to occur during the flooding tide although it may occur under many conditions. The uncoupled portions of the various plumes form patches of coprostanol, PHC, and TSM on the inner shelf adjacent to the bay entrances. The buoyancy/settling characteristics of particles in these patches are a major control of patch persistance. Patches of enriched PHC may be "longer lived" than patches of coprostanol and TSM.

Acknowledgments

This research was partially funded by NOAA grant No. NA-80-FA-D-00007, NASA grant No. NAG1-189, and Old Dominion University. We wish to thank M. Byrnes, K. Gingerich, R. Sawyer, and D. Velinsky for assistance in various phases of this project and J. Haughney for typing the manuscript.

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Annual Input of Petroleum Hydrocarbons to the Coastal Environment via Urban Runoff[1]

EVA J. HOFFMAN, GARY L. MILLS, JAMES S. LATIMER, AND JAMES G. QUINN

Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881, USA

HOFFMAN, E. J., G. L. MILLS, J. S. LATIMER, AND J. G. QUINN. 1983. Annual input of petroleum hydrocarbons to the coastal environment via urban runoff. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 41–53.

To compile an oil pollution budget for Narragansett Bay, Rhode Island, urban runoff samples were collected at four storm drains each serving a different land use. Three to six storm events with different rainfall amounts were monitored at each drain, and the samples were analyzed for petroleum hydrocarbons using glass capillary gas chromatography. The hydrocarbon (HC) load for each storm (mass HC/area) varied systematically with total rainfall, and the storm event load–rainfall relationship was different for each land use. Using rainfall records, the load for each storm was calculated and then summed to predict an annual input rate of hydrocarbons to receiving waters in terms of mass HC/area for each land use. Industrial and interstate highway land gave the highest loads followed by commercial and residential land, respectively. Finally, an estimate of the total hydrocarbon annual input to Narragansett Bay via urban runoff was compiled using land use data from cities and towns in the drainage basin.

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En vue de compiler un bilan de pollution par le pétrole dans la baie de Narragansett, au Rhode Island, nous avons prélevé des échantillons de ruissellement urbain à quatre conduits d'égouts pluviaux, chacun desservant des terres utilisées de manières différentes. À chacun de ces conduits, on a effectué des mesures après trois à six orages avec précipitations différentes. Les hydrocarbures de pétrole ont été mesurés dans les échantillons par chromatographie en phase gazeuse sur capillaire en verre. La charge d'hydrocarbures (HC) (masse de HC/superficie) varie systématiquement en fonction de la hauteur des précipitations, et la relation charge de HC/précipitation diffère selon le type d'utilisation des terres. En se fondant sur les données de pluviosité, on a calculé la charge pour chaque orage, qu'on a ensuite groupée afin de prédire le taux d'apport annuel d'hydrocarbures en termes de masse de HC/superficie correspondant à chaque utilisation des terres. Les terres servant aux industries et aux grandes routes produisent les charges les plus élevées; elles sont suivies des terres commerciales et résidentielles respectivement. En dernier lieu, nous avons estimé l'apport annuel total d'hydrocarbures dans la baie de Narragansett par ruissellement urbain en faisant appel aux données sur l'utilisation des terres des villes situées dans le bassin hydrographique.

Received March 18, 1982
Accepted October 7, 1982

Reçu le 18 mars 1982
Accepté le 7 octobre 1982

PETROLEUM hydrocarbons enter coastal waters from a variety of sources. Although oil spills from tankers (e.g. *Amoco Cadiz* and *Argo Merchant*) and from offshore operations (e.g. Ekofisk and Ixtoc) receive most of the publicity, recent evidence indicates that chronic oil pollution from sources such as sewage treatment plants (Van Vleet and Quinn 1977, 1978) may contribute more oil on a mass basis to coastal waters.

One such potential chronic source of oil pollution to coastal waters is urban runoff. Visual observation of surface slicks on stormwater runoff travelling down curbs into catch basins can only hint that this source should not be ignored. Yet there is limited data on petroleum hydrocarbons in urban runoff

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6845)
Imprimé au Canada (J6845)

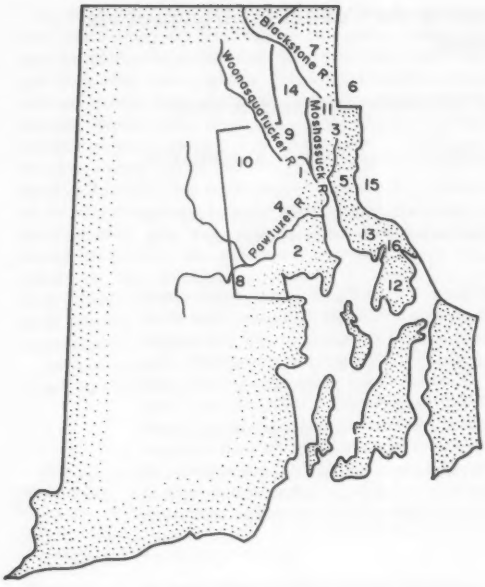


FIG. 1. Rhode Island showing Narragansett Bay and its major tributaries. The upper Narragansett Bay drainage basin considered in this study is outlined and includes the following towns: (1) Providence; (2) Warwick; (3) Pawtucket; (4) Cranston; (5) East Providence; (6) Attleboro, Mass.; (7) Cumberland; (8) W. Warwick; (9) N. Providence; (10) Johnston; (11) Central Falls; (12) Bristol; (13) Barrington; (14) Lincoln; (15) Seekonk, Mass.; and (16) Warren.

(Hunter et al. 1979; Wakeham 1977; Zurcher et al. 1978; Byrne et al. 1980; Eganhouse et al. 1981; Eganhouse and Kaplan 1981; Hoffman et al. 1982). More significantly, there is no method available by which analytical results of petroleum hydrocarbons in effluent collected from one storm drain in a city can be used to estimate the oil discharges one might expect in another area. There are also no data on the relationships of hydrocarbon storm event loads with differing land uses and little data on the storm event loads of hydrocarbons as a function of runoff volume (Hunter et al. 1979).

Therefore, to estimate the annual hydrocarbon input to Narragansett Bay and other coastal waters via urban runoff, we embarked on a program designed to derive (1) hydrocarbon load as a function of rainfall, so that historical records of rainfall could be used to calculate annual inputs; and (2) hydrocarbon loads as a function of land use so that these loads could be estimated anywhere that local land use data are available. This paper outlines the methods used to determine urban runoff loads, presents the relationships of hydrocarbon loads in runoff as a function of rainfall and land use, and illustrates how these relationships can be used to calculate annual inputs of petroleum hydrocarbons to a receiving water body via urban runoff.

Methods and Procedures

DESCRIPTION OF SAMPLING LOCATIONS

Urban runoff samples were collected at four different storm drains each serving a different land use. The specific drains selected for this purpose were chosen on the basis of several criteria. The most important of these are: (1) the drainage basin served by the drain is predominantly one land use type; (2) the drainage system is well charted so that the area served could be calculated; (3) the land use served by the drain is typical of that land use in Rhode Island; (4) the outfall of the drain is not underwater so that discrete sampling is possible from the outfall; and (5) the outfall is accessible with parking nearby and not blocked by fences or steep embankments.

The residential storm drain, the outfall of which is located at the northern end of Manolla Avenue in Warwick, Rhode Island, serves a 0.553 km^2 section of residential neighborhood. The drain, a 91 cm diameter concrete pipe, discharges its effluent into the Pawtuxet River, a tributary of Narragansett Bay (see Fig. 1). The neighborhood is middle class with single family dwellings on lots approximately 1000 m^2 in size. The lawns are grassy and the neighborhood is wooded but not densely so.

The commercial storm drain serves a 0.125 km^2 portion of a shopping center complex in Warwick, Rhode Island. The drain, a 147 cm by 91 cm elliptical corrugated metal pipe, discharges its effluent into the Pawtuxet River. The drainage area is predominantly paved parking lot which gently slopes toward the catch basins. Further details about this sampling site have been reported earlier (Hoffman et al. 1982).

The outfall of the industrial storm drain is located at the intersection of Thurbers Avenue and Allens Avenue in Providence, Rhode Island, and serves a 0.881 km^2 section of an industrial area close to the Port of Providence. The industries located here include metal finishers, oil distributors, and scrap metal dealers among others. The drain discharges its effluent via a 152-cm diameter concrete pipe into the Providence River, a tributary of Narragansett Bay. A small portion of this area (0.014 km^2) is served by a combined sewer which has an overflow into this drain. The slot structure however is in good working condition and there is no evidence of sanitary sewage inputs even under storm conditions.

The highway drain, the outfall of which is located on the Pawtuxet River in Cranston, Rhode Island, serves a 0.448 km^2 section of Interstate 95 and State Route 10. Interstate 95 is an eight-lane highway at this locale and Route 10 is a four-lane highway. Traffic counts in this drainage area averaged 101 500 vehicles/d in 1978 (C. Passarelli, R.I. Dep. of Transportation, Providence, RI, personal communication). The drain, 305 cm in diameter at its outfall, serves the pavement surface and the grassy embankments on each side of the highways. Although there is evidence of groundwater infiltration into this drain, the groundwater contains little petroleum hydrocarbons and does not influence mass balance considerations.

SAMPLING PROCEDURES

Urban runoff samples at each location were collected man-

TABLE 1. Description of storm events studied for urban runoff inputs of hydrocarbons.

Location	Date	Duration of sampling (h)	Rain (cm)	Discharge vol. (L)	Storm description		
					No. of flushes	Flow maximum (L/s)	No. of samples
Commercial	Oct. 24, 1979	3.0	0.13	6.07×10^4	1	21.8	11
Commercial	Apr. 9, 1980	13.0	4.06	3.30×10^6	4	532	10
Commercial	June 28, 1980	4.0	0.30	1.87×10^5	1	24.9	6
Commercial	July 5, 1980	2.0	0.70	5.87×10^5	1	404	7
Commercial	July 8, 1980	1.5	0.51	3.40×10^5	1	247	4
Commercial	July 29, 1980	5.0	3.18	1.84×10^6	4	591	13
Residential	Nov. 3, 1979	18.0	6.76	2.83×10^6	5	173	18
Residential	Oct. 18, 1980	1.5	0.42	7.31×10^5	1	87.6	5
Residential	Apr. 23, 1981	9.5	1.50	7.74×10^5	4	73.8	21
Highway	Nov. 26, 1979	5.0	1.02	1.86×10^7	1	3609	10
Highway	Apr. 28, 1980	2.5	0.64	1.19×10^7	1	2710	5
Highway	Oct. 25, 1980	8.0	3.68	3.97×10^7	2	2591	13
Industrial	May 21, 1980	6.0	1.17	2.90×10^6	1	234	9
Industrial	July 29, 1980	6.0	3.18	2.99×10^6	3[a]	348	6
Industrial	Dec. 3, 1980	1.0	0.05	4.26×10^5	0[b]	118	1
Industrial	Dec. 9, 1980	4.5	0.36	1.08×10^6	1	132	7
Industrial	Feb. 2, 1981	17.0	2.08	8.52×10^6	5	636	27
Industrial	May 12, 1981	16.0	1.04	3.92×10^6	3	485	15
Industrial	June 25, 1981	3.0	0.66	2.79×10^6	2	366	11

[a]First flush missed; data not used.
[b]Drain barely flowed at all; data not used.

ually with a metal bucket from the outfall. Sampling was started at the initiation of rainfall and ended when the drain flow subsided following the end of the storm. Samples were usually collected once every 30 min, more frequently (every 10−15 min) when flow rates were high or rapidly changing, less frequently during quiescent periods. At the time of sample collection drain water height and flow velocity (for drain flow rate calculations), cumulative rainfall readings, and local time were recorded. After collection, the samples were stored in precleaned 4-L amber glass bottles with Teflon lined caps.

A description of the storms we sampled is given in Table 1. Only in one instance was an attempt made to sample a storm simultaneously at two different land uses (July 29, 1980 at the commercial and industrial sites). Usually we concentrated our sampling efforts at one location at a time changing personnel if the storm lasted longer than 12 h.

ANALYTICAL PROCEDURES

Shortly upon return to the laboratory, the runoff samples were filtered through preweighed, precombusted glass fiber filters (Whatman GF/C). After drying at room temperature the filter samples were reweighed to determine the amount of suspended solids in each sample, then frozen until further analysis. Experiments involving settleability and particle size distributions were also performed soon after return of the samples to the laboratory (Hoffman et al. 1982). A 3-L aliquot of each filtrate containing "soluble" hydrocarbons was extracted with 300 mL of dichloromethane in the original sample container. This organic extract was then stored for further analysis.

The filters containing the suspended solids and associated hydrocarbons were analyzed by a technique often used for hydrocarbon analyses in sediments (Hoffman and Quinn 1978). Briefly, the filters were shredded, then extracted with methanol under reflux conditions. After water was added, the nonpolar materials were partitioned from the aqueous-methanol phase into petroleum ether. The hydrocarbons were isolated from the other nonpolar materials in both the "soluble" extract and the filter extract by silica-gel chromatography. Samples in 1 mL of hexane were charged to Pasteur pipets containing ~2 g of fully activated silica gel. Two hydrocarbon fractions were collected: F_1 eluted by 15 mL of hexane contained essentially the saturated hydrocarbons (for example *n*-alkanes, branched alkanes, cycloalkanes), and F_2 eluted by 15 mL of an 80:20 hexane:dichloromethane mixture contained polyunsaturated hydrocarbons and polycyclic aromatic hydrocarbons. Each fraction was then analyzed by glass capillary gas chromatography and quantified using internal standards (nC_{22} for F_1 and anthracene for F_2) added prior to extraction. Concentrations reported for total hydrocarbons are a sum of the F_1 and F_2 fractions of both the particulate and soluble components of each sample. Because blanks contained < 25 μg HC, blank corrections were rarely necessary. The analytical precision of the method based on 14 replicate sediment analyses was ~15% (Hoffman and Quinn 1978).

TERMINOLOGY

To be consistent with urban runoff literature, units in terms of mass/s are called discharge rates; mass·drainage area^{-1}·storm^{-1} are called storm event loads; mass·area^{-1}·

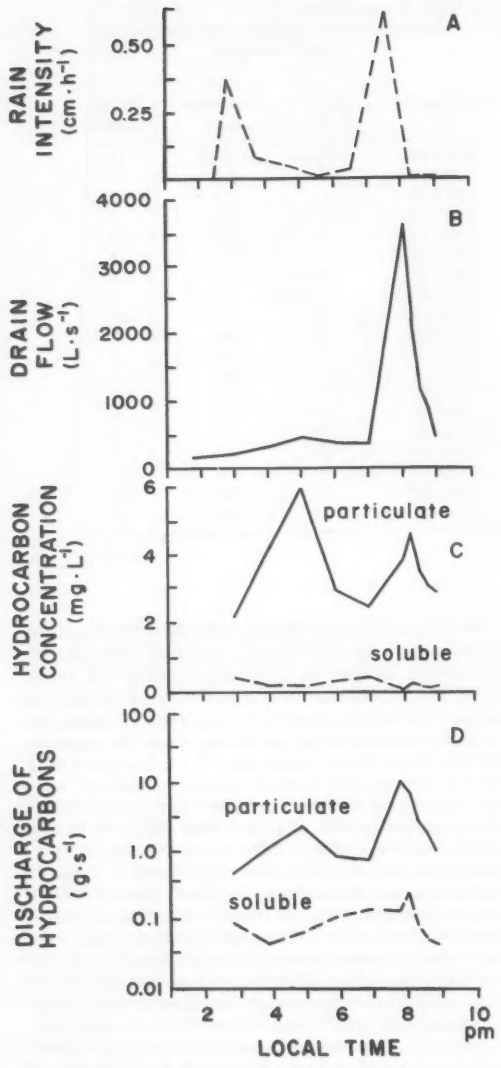


FIG. 2. Rain intensity (A), drain flow rate (B), HC concentrations (C) and HC discharge rate (D) as a function of local time. (Interstate highway sampling site, Nov. 26, 1979.)

time^{-1} are called loads; and mass/yr are called annual inputs. Total hydrocarbons are the sum of both soluble and particulate hydrocarbons.

Results and Discussion

An example of the type of data generated by the extensive storm event monitoring is given in Fig. 2. This storm on Nov. 26, 1979 at the highway location, was characterized by two pulses of rain, the first around 15:00 and the second around 19:00 (Fig. 2A). The flow rate increased slightly as a result of the first rain pulse but increased very rapidly in response to the second rain pulse (Fig. 2B). The small flow rate response to the first rain pulse was noted at other locations as well (Hoffman et al. 1982). A proportion of the first rain pulse is used to wet surfaces and in depression storage before the excess starts to flow over the surfaces toward catch basins. The concentrations of hydrocarbons also varied as a function of time with one peak in concentration occurring during the first slight increase in flow rate and the second peak occurring shortly after the rapid increase in flow began to subside (Fig. 2C). In all cases the soluble hydrocarbon concentrations remained small in comparison to the particulate contribution. Figure 2D shows the variations in discharge rate of hydrocarbons (the product of the concentration and the flow rate). Large peaks in discharge rate can be attributed to high concentrations and/or high flow rates. As can be seen, the hydrocarbon discharge rates in this storm varied by 2 orders of magnitude. Other storms monitored in this study indicate that discharge rates can vary within a storm by 5 orders of magnitude. Because of this large variability, we concluded very early in this project that there was no such thing as a "representative" grab sample for urban runoff. Therefore to estimate properly the discharge rates of any component in urban runoff it is necessary to collect samples encompassing the entire storm event. Storm event mass loads of hydrocarbons for each of 21 different storms were calculated by mathematical integration of the discharge rates in mass HC/unit time over each storm period.

The total mass of hydrocarbons discharged by each drain was divided by the appropriate drainage area to yield storm event loads in mass HC·km^{-2}·storm^{-1} and expressed as a function of rainfall (Fig. 3). It is also possible to relate the loads to volume of total runoff. Since runoff is a function of rainfall, and rainfall data is readily available from the National Weather Service, we have chosen to relate the mass HC·km^{-2}·storm^{-1} to the total rainfall of that storm (Table 2).

In several cases, the relationship could be expressed in either a linear or a polynomial equation (see Table 2). The linear expression implies that as the rainfall increases the hydrocarbon load increases indefinitely, and suggests that the supply of hydrocarbons is never exhausted. Moreover, occasionally the linear form has an intercept which is difficult to interpret physically (i.e. there should be no discharge of hydrocarbons via runoff if there is no rain). Therefore, in some cases, the data could be fit better by a polynomial expression. The data at these land use locations indicated that beyond a certain quantity of rainfall the hydrocarbon storm event load achieved a maximum value which did not increase with additional rainfall, and suggested that the supply of hydrocarbons has been exhausted.

It is interesting to note that there is no indication of curvature for the data obtained at the heavily polluted industrial site (Fig. 3D); whereas the data from the relatively clean residential site showed pronounced curvature (Fig. 3A) with the maximum load being achieved after only 2.5 cm of rainfall.

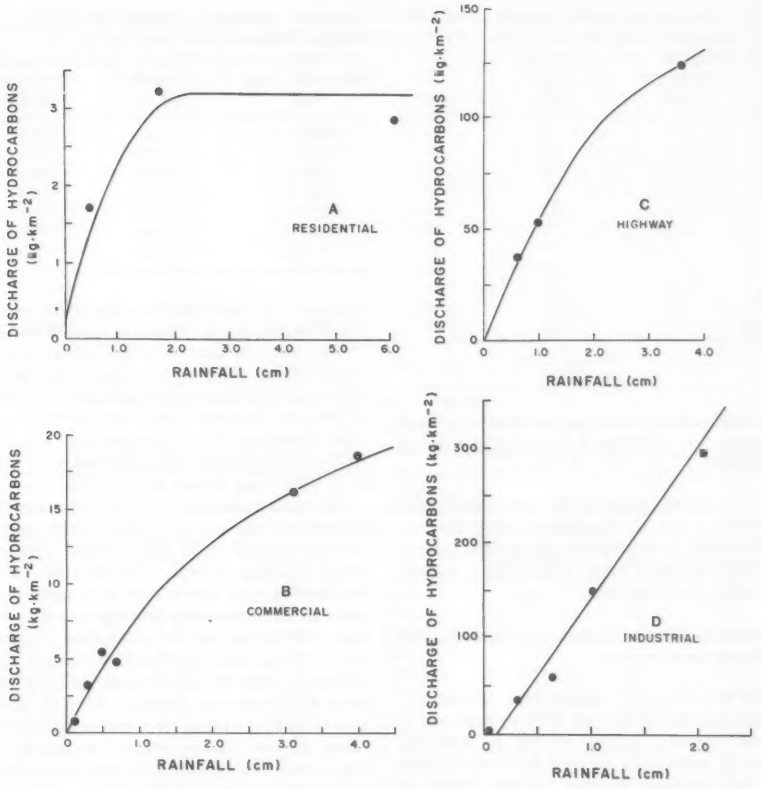


FIG. 3. Mass of hydrocarbons discharged at each land use as a function of storm rainfall amounts (A = residential; B = commercial; C = highway; D = industrial).

TABLE 2. Equations relating hydrocarbon storm loads to storm rainfall.

Polynomial	Linear
Residential	
g HC·km^{-2}·storm^{-1} = 341.3 + 2185 (rain [cm]) − 267.7 (rain [cm])^2 for cm < 2.54 g HC·km^{-2}·storm^{-1} = 4164 for cm > 2.54	Not appropriate
Commercial	
g HC·km^{-2}·storm^{-1} = 463 + 7500 (rain [cm]) − 775 (rain [cm])^2 for cm < 4.8 g HC·km^{-2}·storm^{-1} = 18580 for cm > 4.8	g HC·km^{-2}·storm^{-1} = 4272 rain (cm) + 1807
Highway	
g HC·km^{-2}·storm^{-1} = 1063 + 117110 (rain [cm]) − 14155 (rain [cm])^2 for cm < 4.1 g HC·km^{-2}·storm^{-1} = 252120 for cm > 4.1	g HC·km^{-2}·storm^{-1} = 61000 rain (cm) + 22800
Industrial	
Not appropriate	g HC·km^{-2}·storm^{-1} = 149600 rain (cm) − 17230

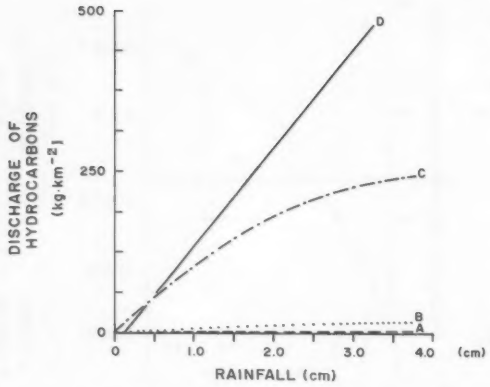


FIG. 4. Mass of hydrocarbons discharged as a function of rainfall amounts and land use; A = residential; B = commercial; C = highway; and D = industrial.

Each land use also differs greatly in the hydrocarbon mass involved. To illustrate this, all the equations using the same scales are shown in Fig. 4. In all storms greater than 0.5 cm, the industrial land discharges more hydrocarbons per unit area than any of the other land uses.

LOADS OF PETROLEUM HYDROCARBONS VIA URBAN RUNOFF AS A FUNCTION OF LAND USE

The mass $HC \cdot km^{-2} \cdot storm^{-1}$ relationships derived as a function of rainfall for each storm (see Table 2) were used in conjunction with historical rainfall records to determine annual urban runoff input loads for each land use. Rainfall records from the National Weather Service station in Warwick, Rhode Island were used for this purpose (Table 3). In summing the amount of rain in each storm, we considered rainfall occurring on successive days with less than 12 dry hours in between as part of the same storm. We also did not consider any storm which had a total rainfall of 0.025 cm or less, because visual observations revealed that no runoff occurred with that little rainfall. Because Rhode Island is a coastal state, most of the annual precipitation occurs as rain with little snow, sleet, or ice. Between 1970 and 1980, rain accounted for 86–99% of the total precipitation, averaging 94% (see Table 4). For this reason we also chose to ignore snowmelt contributions in our annual input calculations. Dynamic considerations concerning the incorporation of oily particles as a function of flow rates over a surface might suggest that pollutants should be washed off streets much more effectively by rainfall than snowmelt. A recent study (Bennett et al. 1981), however, showed that snowmelt can result in similar or higher runoff loads of oil and grease than rainfall, presumably due to splashing of slush underneath cars washing the oily surfaces there. This study was conducted in Colorado where snowfalls are a more significant form of precipitation than in Rhode Island. Since the relationships derived here were based entirely on rainstorm sampling, they are probably inappropriate for snowmelt. In areas where snowmelt is important hydrologically, its contribution to runoff should not be ignored as done in this case.

TABLE 3. Distribution of storm events and rain amounts 1970–80, National Weather Service, Warwick, RI.

Rain/storm event (cm)	Number of rain events	% of total number	% of total volume
0.051–0.25	193	24.0	1.8
0.25–1.27	295	36.6	14.0
1.27–2.54	149	18.5	21.6
2.54–3.81	73	9.1	17.6
3.81–5.08	42	5.2	14.6
5.08–7.62	40	5.0	19.2
>7.62	13	1.6	11.1

The effect of antecedent dry periods on runoff loads is controversial. Some studies suggest that the longer the dry period before the storm, the higher the pollutant load in runoff (Litwin and Anthony 1978). Other studies (i.e. Bedient et al. 1980) found no effect. We chose to ignore this factor in our hydrocarbon input calculations based on the data of Hoffman et al. (1982) and Hunter et al. (1979).

The loads ($mass \cdot km^{-2} \cdot yr^{-1}$) of urban runoff hydrocarbons for each land use area were calculated by computation of each storm event load ($mass \cdot km^{-2} \cdot storm^{-1}$) expected from each storm occurring between 1970 and 1980 and then summing the loads at each land use for each year (Table 5). Annual loads at the commercial and highway sites were calculated using both linear and the polynomial equations. When the 11-yr average was calculated, the results using the linear equations were not significantly different than the results using the polynomial equations. Each of the loads from the various land use types are significantly different from each other, in some cases by orders of magnitude. To our knowledge, loads for different land uses have never before been derived for petroleum hydrocarbons.

Our data indicate that the residential areas have the smallest hydrocarbon loads. The sources of the hydrocarbons on such land are mostly automotive lubricating oil which has dripped onto the road surfaces, and a small but recognizable contribution of plant wax hydrocarbons (see Fig. 5A). The loads of hydrocarbons at commercial areas are also low in comparison with highway and industrial land uses. Automotive crankcase oil appears to be the major source for the commercial area hydrocarbon runoff (see Fig. 5B). The interstate highway hydrocarbon loads are much higher than the residential and commercial areas. Highways are often not listed separately in land use reports. These data suggest that ignoring highway contributions to runoff can lead to serious error. Crankcase oil again appears to be the primary source of hydrocarbons in highway runoff although some plant wax hydrocarbons from adjacent grassy embankments are sometimes present (see Fig. 5C). The heaviest loads found in this study were from industrial areas. A slick, often heavy, was usually associated with this runoff. The chromatograms revealed that crankcase oil was a contributing source here as well, but in addition, there were often large amounts of fuel oil type hydrocarbons. Figure 5D illustrates a sample where fuel oil hydrocarbons predominated. The source of this fuel oil is unknown. There are several bulk oil distributors in this area

TABLE 4. Summary of annual rainfall data 1970–80, National Weather Service, Warwick, RI.

Year	Total precipitation* (cm)	Total rain (cm)	% rain	No. of rain events	Avg. antecedent dry period (days)
1970	115.4	104.4	90	58	6.3
1971	97.6	91.3	94	72	5.1
1972	165.3	106.9	97	90	4.0
1973	122.5	120.8	98	75	4.8
1974	103.3	95.8	93	81	4.5
1975	129.1	121.6	94	73	5.0
1976	117.6	112.4	96	75	4.9
1977	124.1	113.2	91	78	4.7
1978	119.4	102.8	86	61	6.0
1979	147.8	145.9	99	75	4.9
1980	91.7	87.6	95	70	5.2
$\bar{x} \pm \sigma$	121.2±21.3	114.3±22.3	93.9±3.8	73.4±8.8	5.0±0.6

*Total precipitation = snowfall (water equivalent) + rainfall.

TABLE 5. Annual loads of hydrocarbons via urban runoff as a function of year and land use, Rhode Island.

	$g\ HC \cdot m^{-2} \cdot yr^{-1}$					
		Commercial		Highway		
Year/ land use	Residential (polynomial)	Polynomial	Linear	Polynomial	Linear	Industrial (linear)
1970	0.14	0.59	0.54	6.6	7.6	14.6
1971	0.24	0.53	0.50	7.4	7.2	12.5
1972	0.22	0.80	0.85	11.3	11.9	22.5
1973	0.17	0.61	0.65	8.4	9.1	16.7
1974	0.16	0.54	0.55	7.5	7.7	13.0
1975	0.17	0.60	0.65	8.4	9.1	16.9
1976	0.16	0.54	0.61	7.5	8.6	15.5
1977	0.18	0.62	0.64	6.5	8.9	16.1
1978	0.15	0.53	0.55	7.3	7.6	14.3
1979	0.16	0.59	0.75	8.0	10.5	20.4
1980	0.14	0.45	0.49	6.5	6.9	11.7
$\bar{x} \pm$ SD	0.18±0.04	0.58±0.09	0.62±0.11	7.8±1.3	8.6±1.5	14.0±4.6

and a number of industries using fuel oils in their plants. At first, we suspected that our drain might be unrepresentative of industrial areas in general due to these high loads. However, visual inspection of other storm drains in industrial areas in the Port of Providence revealed that they were similarly contaminated. Therefore, the heavy loads reported here can be considered typical of heavily industrialized areas usually concentrated around port facilities. These loads however are inappropriate for application at recently constructed industrial parks with large open areas. The commercial load relationship is probably most appropriate at these locations.

EXAMPLES OF USE OF THE HC LOAD RELATIONSHIPS TO CALCULATE ANNUAL INPUTS FOR A COASTAL WATERSHED: UPPER NARRAGANSETT BAY AND ITS TRIBUTARIES

The annual mass input of hydrocarbons to Narragansett Bay and its tributaries was calculated by multiplying the previously derived loads (mass $HC \cdot km^{-2} \cdot yr^{-1}$) by the area for each land use category in each drainage basin or town. Land use areas for the various towns in the upper Narragansett Bay drainage basin (Table 6) were collected from the planning departments in each town and are the latest figures available. In most cases, the data were collected on a lot by lot basis and are therefore fairly accurate. In Table 6, the data are listed in 10 different broad categories, although some of the larger towns subdivide the data even further. For example, the city of Providence divides the land use data into over 90 separate categories. The method of reporting such data varies from town to town and from state to state. Usually the data could be divided among the 10 land use categories used in Table 6 with little difficulty, but on occasion it was necessary to consult with the town planner when inconsistencies arose.

Because we determined the loads of hydrocarbons at only four of these 10 land uses, it was necessary to assign the remaining six categories to one of the four types we examined. These assignments (Table 7) may be different in other parts of the U.S. The values for land use areas used in the runoff calculations, after application of the previous

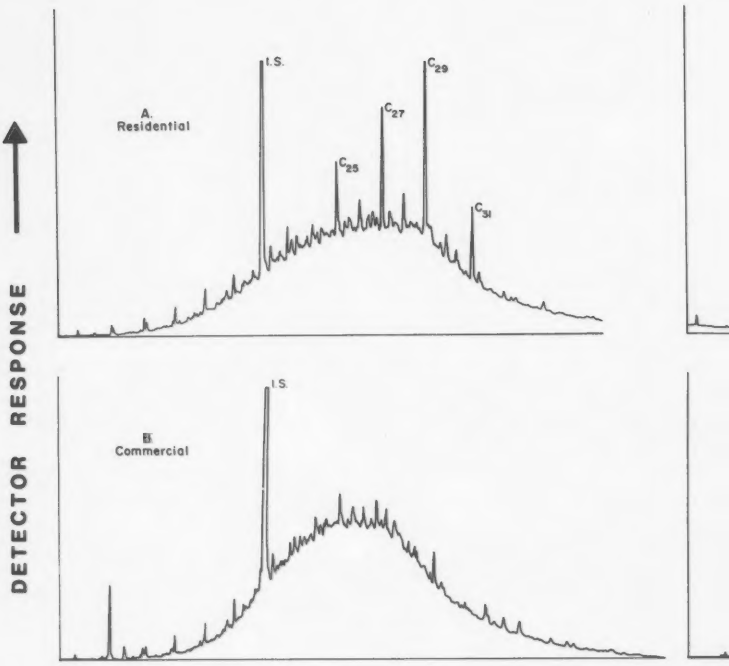
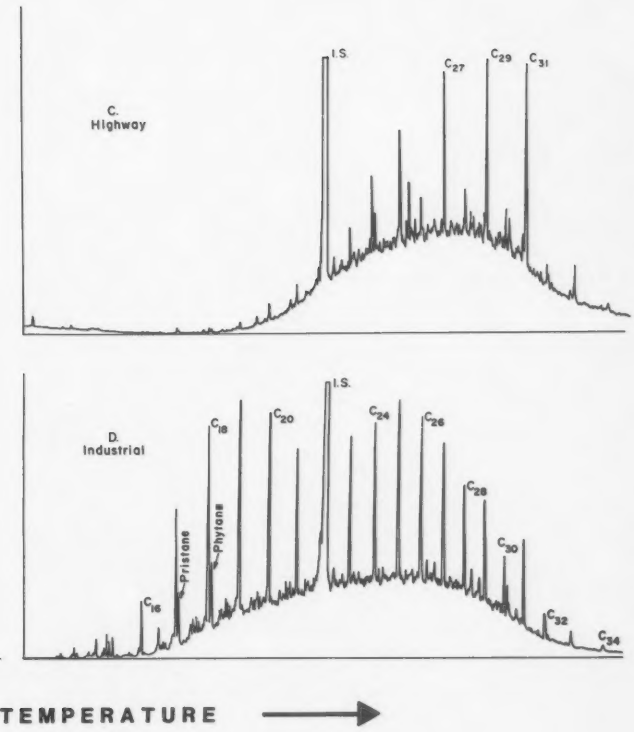


FIG. 5. Gas chromatograms of urban runoff hydrocarbons (particulate phase; F_1 fraction) at different l
in plant waxes, superimposed on an unresolved complex mixture (UCM) typical of petroleum products i
UCM with few resolved components typical of crankcase oils. C = highway illustrating large UCM wi
an *n*-alkane distribution found in fuel oils.



different land uses. A = residential land use illustrating normal odd chain alkanes found products in the boiling range of crankcase oils. B = commercial land uses illustrating large UCM with a contribution of plant wax hydrocarbons. D = industrial showing UCM and

TABLE 6. Summary of land use data in km² by city and town in upper Narragansett Bay drainage basin. (*Included in residential; †also included in other acreages.)

	Resid.	Ind.	Comm.	Inst.	Comm. and util.	Rec. and cult.	Agric. and ext.	Streets and hwy.	Vacant	Water-bodies	Total km²	Pop. (1970)	Pop./ km²
Providence[a]	15.9	2.3	3.2	4.9	3.1	4.0	0.02	12.5	3.1	0.1	49.0	179 116	3655.4
Warwick[b]	33.7	1.3	4.6	8.7	1.7	4.8	—	—*	31.4	—	86.2	83 694	970.9
Pawtucket[c]	8.4	2.1	1.7	2.4	0.8	1.2	—	4.6	1.7	0.3	23.1	76 984	3332.6
Cranston[d]	20.7	1.4	1.6	4.3	0.7	3.0	2.4	6.2	29.7	—	70.0	74 287	1061.2
E. Providence[e]	9.7	1.5	2.0	1.0	3.9	5.4	0.7	4.8	5.1	1.3	35.5	48 207	1357.9
Attleboro[f]	8.8	2.0	0.8	4.3	—	1.6	1.9	6.4	35.8	9.1	71.9	32 907	457.7
Cumberland[g]	12.9	0.8	0.9	1.5	1.1	0.6	5.5	—	45.0	5.4	73.6	26 605	361.5
W. Warwick[g]	8.2	1.0	0.9	0.8	0.4	0.7	1.3	—	7.2	0.9	21.3	24 323	1141.9
N. Providence[g]	7.7	0.3	0.7	0.6	0.1	0.5	0.2	—	4.2	0.5	14.9	24 337	1633.3
Johnston[g]	10.5	0.5	1.1	0.4	1.0	0.3	2.8	—	42.1	4.3	63.0	22 037	349.8
Central Falls[h]	1.7	0.4	0.4	0.2	0.02	0.06	0.02	0.09	0.2	0.3	3.4	18 716	5504.7
Bristol[g]	6.6	0.7	0.5	0.4	0.3	2.0	3.1	—	12.1	1.4	27.2	17 860	656.6
Barrington[g]	12.5	0.1	0.3	0.8	0.3	1.7	0.6	—	4.8	2.0	23.0	17 554	763.2
Lincoln[g]	7.6	1.4	0.5	1.0	1.6	—	1.7	—	29.8	2.0	45.6	16 182	354.9
Seekonk[i]	7.7	0.7	3.6	—	—	2.0	7.2	1.4†	25.2	1.7	48.3	12 500	258.8
Warren[g]	4.0	0.3	0.5	0.3	0.1	0.3	3.3	—	4.7	1.8	15.4	10 523	3758.2
Total	176.6	16.8	23.0	31.7	15.0	29.4	31.0	34.6	282.0	31.1	671.3	685 832	1021.6
Percent	26.38	2.50	3.45	4.15	3.54	4.38	4.63	5.17	41.42	4.38			

[a]City of Providence Department of Planning and Urban Development, "Land Use Comparison, 1975" (George J. Turlo, Supervisor of Current Planning) June 1978.

[b]City of Warwick, Department of City Planning, "Warwick, 1990" 1972.

[c]City of Pawtucket, City Planning Department, "Land Use Inventory and Commentary," (Edward M. Hennigan, City Planning Director) Sept. 1977.

[d]City of Cranston, City Planning Commission, "Land Use Analysis," January 1974.

[e]City of East Providence, Department of Planning and Urban Development "Land Use Analysis: 1973" (Joseph L. Savick, Director) December 1974.

[f]Town of Attleboro, Dep. of Planning, personal communication, 1979.

[g]208 Land Use Summaries, U.S. Dep. of Housing and Urban Development.

[h]Howe, Spencer, Principal Planner, Dep. of Community Affairs, State of Rhode Island, personal communication, December 1979.

[i]Town of Seekonk Planning Board, "A Master Plan for the Town of Seekonk," May 1979.

assumptions, are presented in Table 8. The highway areas had to be estimated independently since some towns did not list this category at all and others included all the town streets into a category "streets and highways." When this figure was reported at all, it was usually obtained by difference (that which was left over when all the other land uses were summed). In our study, streets contributed to the runoff at the various different land use areas. A separate consideration of the streets would have led to their inclusion twice. To circumvent this problem we measured the length of interstate highways and other multilane highways in each town, and based on the interstate plans at our sampling location, assigned an average width of 76 m. The areas were then calculated on that basis. Only one town, Pawtucket, reported a separate land use area for their interstate highway. They reported that I-95 occupied 0.518 km² in their city. The estimate calculated by our method indicated an area of 0.449 km² for this section; this difference of 15% is acceptable for our purposes.

To estimate the runoff contributions to each tributary of upper Narragansett Bay, it was necessary to know the land use regimes in each watershed. Land use assignments for the various watersheds were reported by Graber (1978) for Rhode Island. After correction for the slightly different total land areas considered, close examination of the total land use areas in the various categories did not agree with the values obtained for the same categories as determined by each town and city. This is probably due to at least two factors: (1) The towns and cities generated their data on a lot by lot basis and were verified by visual inspection; whereas, the watershed data (Graber 1978) was estimated using 1970 aerial photographs using much less detail than reported by cities and towns; (2) The towns and cities use different categories than those used in the watershed analysis. For example, the parks and playgrounds were classified in the "recreational and cultural" category (which we considered to be most like the residential category with respect to runoff). The watershed information includes this in the "vacant and open" category. After consultation with various local community planners, the data generated by the cities and towns were judged to be the most accurate data. It also appears to be the most recent data since the watershed data, although published in 1978, were based on 1970 photographs. Therefore, in order to have the total runoff values as tabulated by watershed equal the total runoff values as tabulated by cities and towns, it was necessary to adjust the watershed data. For example, if the total residential use from the town data was 15% higher than the

TABLE 7. Land use categories, as reported by cities and towns (Table 6), divided among land use categories for runoff calculations.

Land use categories as listed by cities and towns	Land use categories assigned for runoff calculation purposes	Notes
Residential	Residential	
Industrial	Industrial	
Commercial	Commercial	
Institutional	Commercial	Includes hospitals, schools, etc. Traffic pattern similar to commercial.
Transportation, communication and utilities	Industrial	Includes power plants, bulk oil terminals, bus and railway stations, etc. Traffic pattern similar to industrial areas.
Recreational and cultural	Residential	Includes parks and cemeteries.
Agricultural and extractive	Not considered for petroleum runoff	Farms and quarries.
Streets and highways	Highways estimated separately, streets as a part of other land uses (see text)	These data are usually calculated by difference, and highways are not considered separately. The highway contribution had to be estimated and the street portion was considered as a part of other land uses.
Vacant	Not considered for petroleum runoff	
Water bodies	Not considered for petroleum runoff	

TABLE 8. Land use areas by river and drainage basins; (corrected by town data and balanced by open land adjustment). Land use areas (km^2).

	Resid.	Comm.	Ind.	Hwy.	Open	Total
Blackstone River/ Seekonk River	45.18	9.94	7.65	2.70	247.45	312.93
Pawtuxet River	48.49	17.04	7.96	8.37	20.64	102.49
Providence River/ Upper Bay	53.38	15.31	8.03	6.13	0	83.86
Moshassuck River	21.23	5.73	5.02	1.49	20.59	54.05
Woonasquatucket River	36.73	6.74	3.13	0.96	74.32	121.88
Total	206.01	54.77	31.79	19.64	362.99	675.20

watershed totals, residential area in each watershed was increased by 15%. Open land was used to balance the individual watershed subtotals. The land use data for watersheds, as reported by Graber (1978) and corrected for consistency purposes are given in Table 9. This obviously serves only as a first approximation attempt. The watershed inputs should be recalculated when better watershed land use data become available.

A summary of the total annual input of hydrocarbons for each area was calculated by multiplying the appropriate loads (mass $HC \cdot km^{-2} \cdot yr^{-1}$) and the corresponding land use areas. The annual inputs for each city and town are given in Table 10, and for each tributary watershed in Table 11. The total annual input of hydrocarbons via urban runoff to the upper Narragansett Bay watershed was calculated to be 665 t HC/yr. In every city and town examined here, the hydrocarbon inputs from industrial areas exceeded the inputs from any other land use. In fact, the inputs from industrial land uses represent, on a town by town basis, from 44 to 90% (averaging 67%) of the total hydrocarbon runoff inputs. The highways are the second most significant source of hydrocarbons in runoff in the upper Narragansett Bay drainage basin. Total highway inputs represent about 23% of the total hydrocarbon runoff. Residential and commercial areas in the drainage basin contribute only 5.4 and 4.8%, respectively (see Table 9).

RELATIONSHIPS OF HYDROCARBON ANNUAL INPUTS TO DEMOGRAPHIC PARAMETERS

Regression analysis of annual hydrocarbon inputs via runoff versus town population revealed only a weak relationship. Relationships of runoff inputs and number of registered vehicles, number of private businesses, and number of manufacturing firms in each town were also poor. The best relationship found was between hydrocarbon inputs via urban runoff

TABLE 9. Land use areas for urban runoff calculations. Combination of land use data from town planning offices (Table 6) adjusted using assumptions (Table 7) except where noted.

	Residential	Commercial	Industrial	Highway[a]
			km^2	
Providence	19.94	7.99	5.37	2.22
Warwick	38.43	13.30	3.02	4.82
Pawtucket	9.63	4.08	2.90	0.75
Cranston	23.71	5.87	2.12	3.08
E. Providence	15.14	3.05	5.41	2.50
Attleboro	11.59	5.11	1.99	1.27
Cumberland	13.43	2.38	1.86	0.31
W. Warwick	8.93	1.65	1.35	0.54
N. Providence	8.23	1.35	0.39	—
Johnston	10.79	1.46	1.49	2.52
Central Falls	1.79	0.61	0.43	—
Bristol	8.64	0.93	0.95	—
Barrington	14.18	1.10	0.32	—
Lincoln	7.60	1.50	2.97	1.25
Seekonk	9.70	3.63	0.73	0.35
Warren	4.32	0.78	0.46	—
Total	206.04	54.79	31.79	19.64

[a]Estimated from highway lengths in each town (see text).

TABLE 10. Mass loads of hydrocarbons in urban runoff by cities and towns in the upper Narragansett Bay watershed (towns listed by decreasing population).

	Residential	Commercial	Industrial	Highway	Total
			Annual hydrocarbon loads (t/yr)		
Providence	3.51	4.65	75.17	17.28	100.61
Warwick	6.76	7.74	42.28	37.45	94.23
Pawtucket	1.69	2.38	40.53	5.87	50.47
Cranston	4.17	3.41	29.61	23.91	61.10
E. Providence	2.66	1.77	75.62	19.45	99.50
Attleboro	2.04	2.98	27.79	9.90	42.71
Cumberland	2.36	1.38	26.04	2.39	32.17
W. Warwick	1.57	0.96	18.85	4.18	25.56
N. Providence	1.45	0.79	5.49	—	7.73
Johnston	1.90	0.85	20.88	19.60	43.23
Central Falls	0.31	0.36	6.00	—	6.67
Bristol	1.52	0.54	13.30	—	15.36
Barrington	2.49	0.64	4.86	—	7.99
Lincoln	1.34	0.87	41.55	9.71	53.47
Seekonk	1.71	2.11	10.19	2.76	16.77
Warren	0.76	0.45	6.51	—	7.72
Total	36.25	31.88	444.70	152.47	665.30
Percent	5.4%	4.8%	66.8%	22.9%	100.0%

and vehicle km/d estimated for each town by Statewide Planning (1981). The equation, however, is difficult to interpret physically; and the relationship may arise from land use considerations used in estimating the vehicle km/d values.

Our data demonstrate that urban runoff inputs of hydrocarbons cannot be related to population on an intrametropolitan district scale. This probably happens because the towns within a metropolitan district can have different land use regimes. One town may be primarily a suburban community whose people commute to a nearby city where the industry is located. The population for the watershed we examined was 686 000 people. Our estimate of urban runoff inputs expressed on a per capita basis is 0.969 kg HC·capita^{-1}·yr^{-1}. Only one other study has expressed hydrocarbon urban runoff in those units. Eganhouse et al. (1981) estimates a mass emission rate of 0.875 kg HC·capita^{-1}·yr^{-1} for the Los Angeles River drainage basin with a population of approximately 3 million.

TABLE 11. Mass loads of hydrocarbons in urban runoff by watersheds.

	Residential	Commercial	Industrial	Highway	Total
	Annual hydrocarbon loads (t/yr)				
Blackstone River/ Seekonk River	7.95	5.79	107.04	20.92	141.70
Pawtuxet River	8.53	9.92	111.29	64.94	194.66
Providence River/ Upper Bay	9.57	8.91	112.36	47.60	178.44
Moshassuck River	3.74	3.33	70.19	11.53	88.79
Woonasquatucket River	6.46	3.92	43.76	7.48	61.62
Total	36.24	31.87	444.65	152.47	665.23

The close agreement between these annual per capita inputs suggests that urban runoff hydrocarbon loads and population may be related on an interregional scale. The agreement is especially interesting since these two values were derived using different approaches in areas with entirely different climatologies. However, further data from other regions will be necessary to resolve for certain whether population can be used to normalize runoff inputs on an interregional scale.

PROJECTED ANNUAL INPUT OF HYDROCARBONS VIA URBAN RUNOFF TO U.S. AND WORLD COASTAL WATERS

Comparison of the 665 t/yr input of hydrocarbons with other sources of oil to the Narragansett Bay watershed suggests that urban runoff is a major source of hydrocarbons (~40%) to Narragansett Bay and its tributaries (E. J. Hoffman unpublished data). Projection of our data to U.S. or worldwide oil pollution budgets requires a number of assumptions. The National Academy of Sciences (1975) analysis stated that urban runoff constituted 15–90% (average 50%) of the inputs contributed by municipal and industrial wastewater sources. Then using a municipal and wastewater input rate of 8 $g \cdot capita^{-1} \cdot d^{-1}$ and a coastal zone population in the U.S. of 68 million (NAS 1975) they estimated a U.S. coastal input from urban runoff of 100 000 t/yr and a worldwide urban runoff input of 300 000 t/yr. Our data indicate a 0.969 kg $HC \cdot capita^{-1} \cdot yr^{-1}$ input for urban runoff hydrocarbons which, given the 68 million coastal population of the U.S. (NAS 1975), would project a U.S. coastal water hydrocarbon urban runoff input of 66 000 t/yr urban runoff and 198 000 t worldwide. Considering that our assumptions and those of the NAS (1975) are different, the degree of agreement between the two estimates is remarkable but quite possibly fortuitous.

Acknowledgments

This work was funded by a U.S. National Oceanic and Atmospheric Administration's Office of Marine Pollution Assessment (NOAA–OMPA) Grant No. NA80RAD00047. We thank the public works, planning and engineering departments of the cities of Providence, Warwick, Cranston, East Providence, and Seekonk, the Rhode Island Departments of Transportation, Environmental Management, and Statewide Planning, the U.S. Environmental Protection Agency's Environmental Research Laboratories in Edison, NJ and Narragansett, RI and Region I Water Resources Offices in Boston, MA, for sewer maps, engineering plans, land use data and helpful suggestions in the design of this project. We especially thank Lynne Hanson and Candace Oviatt of Marine Ecosystems Research Laboratory, URI; Donald Robadue of the Coastal Resources Center, URI; Anne Falke of the Chemistry Department, URI; and Adolpho Requejo, URI, for aid in sample collection and data reduction. We further thank WJAR Channel 10 meteorologists and meteorologists from the National Weather Service in Warwick, RI for personalized service in behalf of our studies.

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Suspended Load and Solubility Affect Sedimentation of Petroleum Hydrocarbons in Controlled Estuarine Ecosystems[1]

J. N. GEARING AND P. J. GEARING

Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881, USA

GEARING, J. N., AND P. J. GEARING. 1983. Suspended load and solubility affect sedimentation of petroleum hydrocarbons in controlled estuarine ecosystems. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 54–62.

The concentrations of No. 2 fuel oil and a suite of hydrocarbons with varying chemical properties (perhydrofluorene, pristane, biphenyl, 1-methylnaphthalene, 9-methylanthracene, and pyrene) were measured over time in the water column, on suspended particles, and in the sediments of two controlled microcosms receiving different amounts of mixing energy. The initial aqueous concentrations of the No. 2 fuel oil and other hydrocarbons were 330–500 μg/L and 0.80–10.8 μg/L, respectively. The levels of suspended particles were 3–5 mg/L in the control microcosm and up to 160 mg/L in the highly mixed system. The simulated storm made no major difference in the overall fate of the hydrocarbons. The concentration on particles collected in sediment traps was considerably lower in the tank with high suspended loads, and roughly equal amounts of hydrocarbons were eventually measured in the sediments of each microcosm. The percentage sedimented and residence time in the sediment varied with the lipophilicity and degradability of each hydrocarbon. Fifty percent or more of the least soluble hydrocarbons (aromatics with three or more rings, and saturates) were transported to the sediments. Most of the saturates were more persistent in the sediment than the two-ring aromatics. Aromatics of this class with additional substituent aliphatic groups showed increases in their degrees of sorption and sedimentary residence times in a regular manner. Three- and four-ringed aromatics were similar to the saturates in their sedimentary behavior. After 23 wk, the sediments contained a reduced but still significant fraction (~1/7) of the added petroleum hydrocarbons, enriched in branched and cyclic saturates and high molecular weight aromatics.

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On a mesuré pendant une certaine période les concentrations de mazout n° 2 et d'une série d'hydrocarbures de diverses propriétés chimiques (perhydrofluorène, pristane, biphényle, 1-méthylnaphthalène, 9-méthylanthracène et pyrène) dans la colonne d'eau, sur les particules en suspension et dans le sédiment de deux microcosmes standardisés recevant différentes quantités d'énergie mélangeuse. Les concentrations aqueuses initiales de mazout n° 2 et des autres hydrocarbures sont de 330–500 et 0,80–10,8 μg/L respectivement. Les niveaux de particules en suspension sont de 3–5 μg/L dans le microcosme témoin et jusqu'à 160 μg/L dans le système fortement mélangé. Une tempête simulée n'a pas d'effet majeur sur le sort général des hydrocarbures. La concentration des particules recueillies dans des trappes à sédiment est beaucoup plus faible dans le bassin contenant de fortes charges de matières en suspension tandis que, dans les sédiments de chaque microcosme, des quantités à peu près égales d'hydrocarbures sont éventuellement mesurées. Le pourcentage de matière déposée et le temps de résidence dans le sédiment varient en fonction des propriétés lipophiliques et dégradables de chaque hydrocarbure. Cinquante pour cent ou plus des hydrocarbures les moins solubles (les carbures aromatiques à trois noyeux ou plus et les carbures saturés) sont apportés au sédiment. La plupart des carbures saturés demeurent plus longtemps dans le sédiment que les carbures aromatiques à deux noyaux. Ces derniers, ainsi que des groupes aliphatiques de substitution supplémentaires, montrent des augmentations du degré

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6846)
Imprimé au Canada (J6846)

de sorption et des temps de résidence dans le sédiment comme à l'accoutumée. Les carbures aromatiques à trois et quatre noyaux se déposent de la même manière que les carbures saturés. Après 23 semaines, le sédiment contient une fraction réduite mais significative (~1/7) des hydrocarbures de pétroles ajoutés, enrichis en carbures ramifiés et cycliques et en carbures aromatiques de poids moléculaire élevé.

Received March 18, 1982
Accepted September 27, 1982

Reçu le 18 mars 1982
Accepté le 27 septembre 1982

SEDIMENTATION can be a quantitatively important process for the removal of petroleum hydrocarbons from the water column in estuaries and coastal waters (Blumer and Sass 1972; Meyers and Quinn 1973; Van Vleet and Quinn 1977; and many others), yet relatively little is known about the way it occurs. Current theory (e.g. Karickhoff et al. 1979) suggests that under certain conditions, the extent of sorption may be estimated by a knowledge of the lipophilicity of the sorbate (often measured as the aqueous solubility or octanol–water partition coefficient) and the organic carbon contents and particle size spectrum of the sorbent. Unfortunately, one of the conditions required for an estimation by a simple equilibrium model is that the concentration of sorbate be less than half of its aqueous solubility (Karickhoff 1981), and the solubility of many petroleum hydrocarbons in water is extremely low (Sutton and Calder 1974) and often exceeded due to the presence of discrete oil micelles in the water column.

One way around the difficulty of predicting from theory the sedimentation of oil under "field conditions" is the use of "living models." Microcosms can be effectively used to study the fate of petroleum hydrocarbons (Gordon et al. 1976; Hagstrom 1977; Lee et al. 1978), making possible quantitative determinations of overall rates of pollutant transport under a wide variety of environmental conditions. The Marine Ecosystems Research Laboratory (MERL) at the University of Rhode Island has large-scale microcosms designed to mimic temperate estuaries. While some processes may not operate completely naturally in these microcosms, studies of many parameters, including turbulence, annual nutrient cycles, benthic species composition, gas-exchange rates, annual phytoplankton production and respiration, particle settling and resuspension rates, and phytoplankton species composition, indicate that the divergence is often slight (Nixon et al. 1980; Pilson et al. 1980; Grassle et al. 1980–81; Bopp et al. 1981; Oviatt et al. 1981a; Santschi et al. 1982; Vargo et al. 1982). Several experiments have made use of the MERL microcosms to study the fate of petroleum hydrocarbons in the marine environment. Two experiments were conducted to determine the long-term chemical fate (Gearing et al. 1979, 1980; Wade and Quinn 1980) and biological effects (Berman and Heinle 1980; Elmgren et al. 1980; Grassle et al. 1980–81; Vargo 1981; Vargo et al. 1982) of chronic, low levels of No. 2 fuel oil. To investigate some of the shorter-term processes occurring in the water column, a series of single addition experiments was conducted with individual hydrocarbons and No. 2 fuel oil dispersions under varying environmental conditions (Hinga et al. 1980; Bopp et al. 1981; Gearing and Gearing 1982a, b; Lee et al. 1982; Wakeham et al. 1982).

This study used the facilities at MERL to quantify the effect on hydrocarbon sedimentation of hydrocarbon solubility and suspended particle concentration. In particular, since many accidental oil spills occur in rough weather, the sedimentation of different groups of petroleum hydrocarbons was measured during a simulated storm and compared with sedimentation in a much less turbulently mixed ecosystem.

Materials and Methods

The MERL microcosms, cylindrical fiberglass cylinders 2 m in diameter and 5.5 m in height, can be operated with sediments, seawater, and the associated biota for at least 2 yr. The water temperature can be regulated to 1° at ±10°C of ambient, the flow rate of water can be varied, different degrees of mixing can be provided in each tank and thermoclines and pycnoclines can be maintained. Detailed descriptions of some chemical and biological parameters of the tanks during past experiments are given in Pilson et al. (1977, 1979, 1980).

The two microcosms used in this experiment each contained about 20 cm (depth) of silty-clay surface sediment from mid-Narragansett Bay, together with approximately 13 000 L of bay water and its associated plankton. The temperature of both water columns was similar to that of the bay, 20°C initially (September 1980), 16°C after 2 wk, and 0°C at the end of the experiment (February 1981). Each microcosm was mixed by a plunger suspended from an arm. Throughout the experiment the control microcosm was mixed at five revolutions of the arm per minute (rpm) for 2 h, followed by no mixing for four (Nixon et al. 1980). To simulate a storm of fairly high turbulence and suspended load, during the first 14.5 h the experimental microcosm was mixed at 5 rpm when the mixer of the control tank was operating, and at 14 rpm when it was not. After this time, the mixing rate and schedule were the same in both tanks. The chemical and biological changes which resulted from a similar storm experiment in 1979 were all of short duration (Oviatt et al. 1981b).

As identically as possible, single additions of hydrocarbons were made to each tank while they were being mixed (Table 1). For each addition, approximately 40 L of a hydrocarbon–seawater dispersion were prepared. The same No. 2 fuel oil used in previous MERL oil experiments was combined with two saturated hydrocarbons, perhydrofluorene and pristane, and then mixed vigorously with seawater from the microcosms in a volume ratio of 1:1000 to form a dispersion. The aqueous phase of the dispersion was drawn off, and a mixture of aromatic hydrocarbons (biphenyl, 1-methylnaphthalene, 9-methylanthracene, and pyrene, dissolved in 10–20 mL of acetone) was added to it. The combined hydrocarbon–seawater–acetone mixture was added slowly

TABLE 1. Maximum concentrations of hydrocarbons measured in the water column of, and calculated amounts added to, the storm and control microcosms. Volume of water in each microcosm was 13 000 L.

Hydrocarbon	Storm microcosm		Control microcosm	
	Concentration (μg/L)	Amount added (g)	Concentration (μg/L)	Amount added (g)
ΣF_1	350.	4.56	210	2.70
pristane	8.15	0.106	7.42	0.0965
n-hexadecane	10.8	0.140	5.54	0.072
perhydrofluorene	4.22	0.0549	4.37	0.0568
ΣF_2	143	1.86	120	1.56
2-methylnaphthalene	4.70	0.061	5.50	0.0715
1-methylnaphthalene	5.22	0.068	6.10	0.079
biphenyl	6.74	0.088	7.42	0.096
C_2-naphthalenes	10.0	0.130	10.6	0.138
C_3-naphthalenes	6.45	0.084	5.32	0.069
9-methylanthracene	0.80	0.0104	2.26	0.029
pyrene	8.60	0.112	3.65	0.047

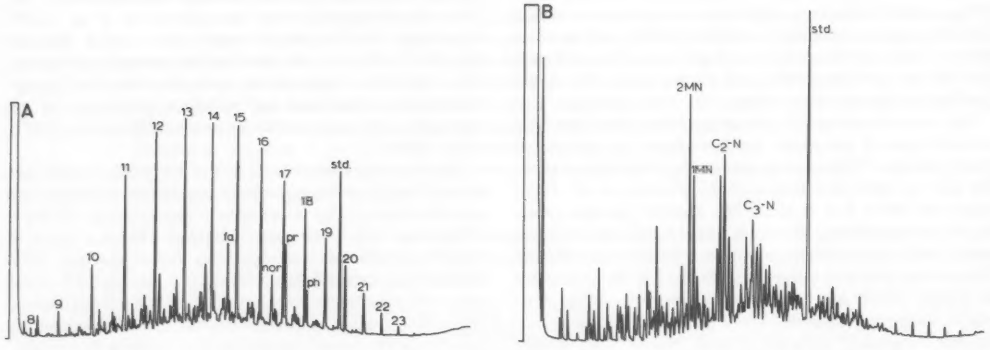

FIG. 1. Gas chromatograms of the F_1(A) and F_2(B) fractions extracted from a dispersion of No. 2 fuel oil with seawater. Numbers indicate the carbon numbers for the *n*-alkane peaks. Internal standards (3-methylnonadecane and phenanthrene) are labeled "std." The isoprenoid hydrocarbons farnesane, norpristane, pristane, and phytane are denoted by fa, nor, pr, and ph. 2MN, 1MN, C_2-N, and C_3-N indicate peaks of the compounds 2-methylnaphthalene, 1-methylnaphthalene, naphthalene isomers with two substituent carbon atoms, and naphthalene isomers with three, respectively.

to each tank (a separate mixture was made up for each), about 1 m below the water surface. No slick was observed. Full descriptions of No. 2 fuel oil–seawater dispersion preparation and addition as well as the chemical composition of the oil used have been published (Gearing et al. 1979, 1980). The dispersion (Fig. 1) was chemically similar to the whole oil except that it contained about 30% instead of 20% aromatics.

Concentrations of suspended matter were measured by filtering a known volume of water onto preweighed Nuclepore filters which were then dried and reweighed. For determination of total organic carbon (carbonate-free), sediment trap material was acidified with HCl, washed with freshwater, filtered onto glass fiber filters (Gelman A/E), dried at < 40°C, and powdered. Weighed aliquots were combusted in a LECO radio-frequency furnace and the evolved CO_2 measured manometrically (Parker et al. 1972).

In sampling the microcosms for hydrocarbons, water was siphoned into clean, solvent-rinsed, glass separatory funnels; suspended material was collected in cylindrical sediment traps. For each sediment sample, 12 cores (2.5 cm in diameter) were collected at random to minimize inhomogeneity. No location was sampled twice. The open-barrelled, stainless steel corer quantitatively samples the entire sediment, including the unconsolidated surface flocculent layer. Sections of the same depth interval from the 12 cores were combined and analyzed as one sample.

For hydrocarbon analyses, internal standards (3-methylnonadecane and phenanthrene) were added to all samples. Total hydrocarbons in water samples were extracted with petroleum ether. Hydrocarbons were extracted from sus-

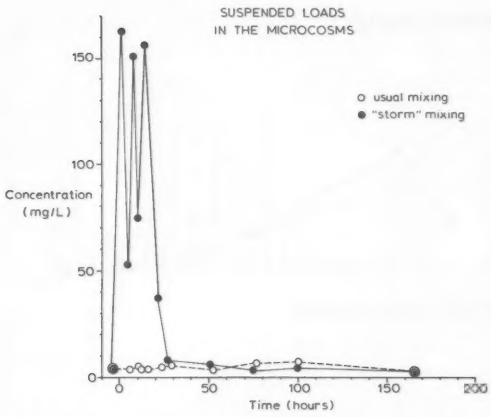

FIG. 2. Concentration of suspended particulate material over time in the water columns of the experimental (solid dots) and control (open circles) microcosms. Data are from filtered water samples. Time is calculated in hours after the organic addition.

pended material and sediments by refluxing the samples with 0.5 mol KOH/L in CH_3OH plus 10% (v/v) H_2O. Extracts were partitioned into petroleum ether. The concentrated extracts of all samples were purified and split into two fractions by column chromatography (1:1 w/w alumina over silica gel). The F_1 (saturated hydrocarbons and olefins with one or two double bonds) and F_2 (aromatic hydrocarbons) fractions were analyzed separately by glass capillary gas chromatography (SE-52, 25 m × 0.25 mm column), using temperature programming (40° to 260° at 4°C/min, 4-min initial hold, or 60° to 245° at 4°C/min, 4-min initial hold) in a Carlo-Erba Series 4160 instrument equipped with a flame ionization detector. Quantification was by comparison with internal standards, using both hand-measured peak heights and electronic measurement of peak areas. Hydrocarbon concentrations in the sediment before the addition were subtracted as blanks. Replicabilities of water and sediment samples were within 10 and 25% of the means, respectively. Details of the sampling and analytical techniques as well as replicability experiments were reported in Gearing and Gearing (1982a) and Gearing et al. (1978, 1979, 1980).

The total amount of hydrocarbon in a microcosm water column at a given time was determined by multiplying the amount of hydrocarbon in a water sample by the ratio of the water column volume to the sampled volume. Similarly, the total amount of hydrocarbon in a microcosm sedimentary compartment was calculated by multiplying the amount measured in core samples by the ratio of the sediment area to the sampled area.

Results and Discussion

WATER COLUMN

The rapid mixing in the experimental microcosm intermittently raised the concentration of suspended solids from 3 to 4 mg/L to over 160 mg/L (30 times the concentration, by weight, of particles in the control tank) for about 24 h (Fig. 2). In a previous study with a microcosm subjected to such mixing (Oviatt et al. 1981b), the concentrations of metals, nutrients, and meiofauna in the water column were raised for a similar time period. We suspected that the suspended matter would be changed qualitatively as well as

TABLE 2. Half lives (hours) of hydrocarbons in MERL water columns ($C = C_o e^{-kt}$, $t_{1/2} = \frac{\ln 2}{k}$) in the presence of varying amounts of resuspended sediment. Water column temperatures in all three experiments were around 20°C.

Hydrocarbon	September, 1979 no sediments regular mixing	September, 1980 sediments regular mixing	September, 1980 sediments rapid mixing
ΣF_1	37	46	31
n-tetradecane	23	27	19
n-hexadecane	23	29	21
n-octadecane	—	33	24
n-eicosane	29	34	25
n-docosane	33	41	25
n-tetracosane	32	—	19
norpristane	37	42	24
pristane	—	47	27
perhydrofluorene	—	39	29
ΣF_2	22	45	34
2-methylnaphthalene	15	17	20
biphenyl	—	21	21
C_2-naphthalenes	—	28	32
C_3-naphthalenes	—	34	38
9-methylanthracene	—	51	43
pyrene	—	59	33

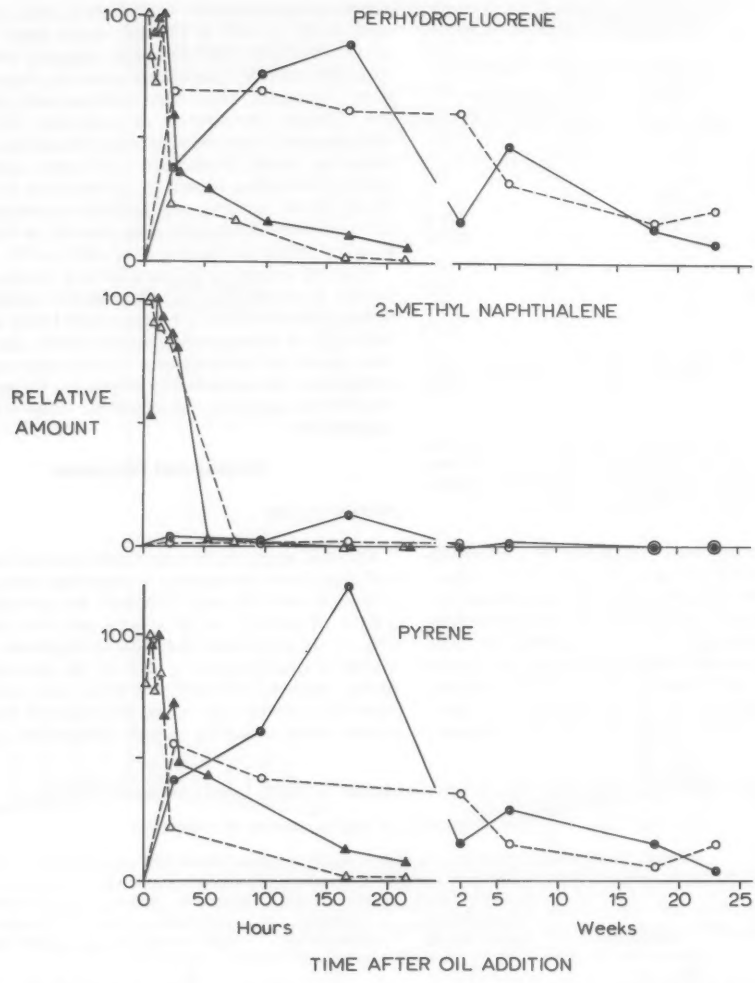

FIG. 3. Relative amounts versus time for representative compounds in the experimental (solid lines) and control (dashed lines), microcosms. △−▲ indicate amounts in water samples, and ○−● amounts in sediment samples. Amounts are normalized to the maximum added to the water column (Table 1).

quantitatively, with an increase in resuspended silty-clay particles from the sediments relative to organic detritus produced in the water column. Although microscopic examination revealed this to be the case, there was no significant difference between the control and experimental microcosms in the total organic carbon contents of particles collected in sediment traps, both averaging 27 mg/g.

One of the hypotheses to be tested in this experiment was that the resuspended matter in the storm microcosm would greatly affect the rates of removal of hydrocarbons from the water column. Increased disappearance rates of some metals in summer compared to winter have been postulated to result from increased particle flux and resuspension in warm weather (Santschi et al. 1980). In contrast, aqueous residence times of hydrocarbons were quite similar in slowly mixed, summer experiments with and without sediments at the bottom (Table 2), implying that organic detritus produced in the water was more important in the sedimentation of such compounds than resuspended mineral particles. The simulated storm resulted in slightly shorter hydrocarbon half lives overall, with less variation in removal rate with chemical properties than had been observed previously (Table 2). Pos-

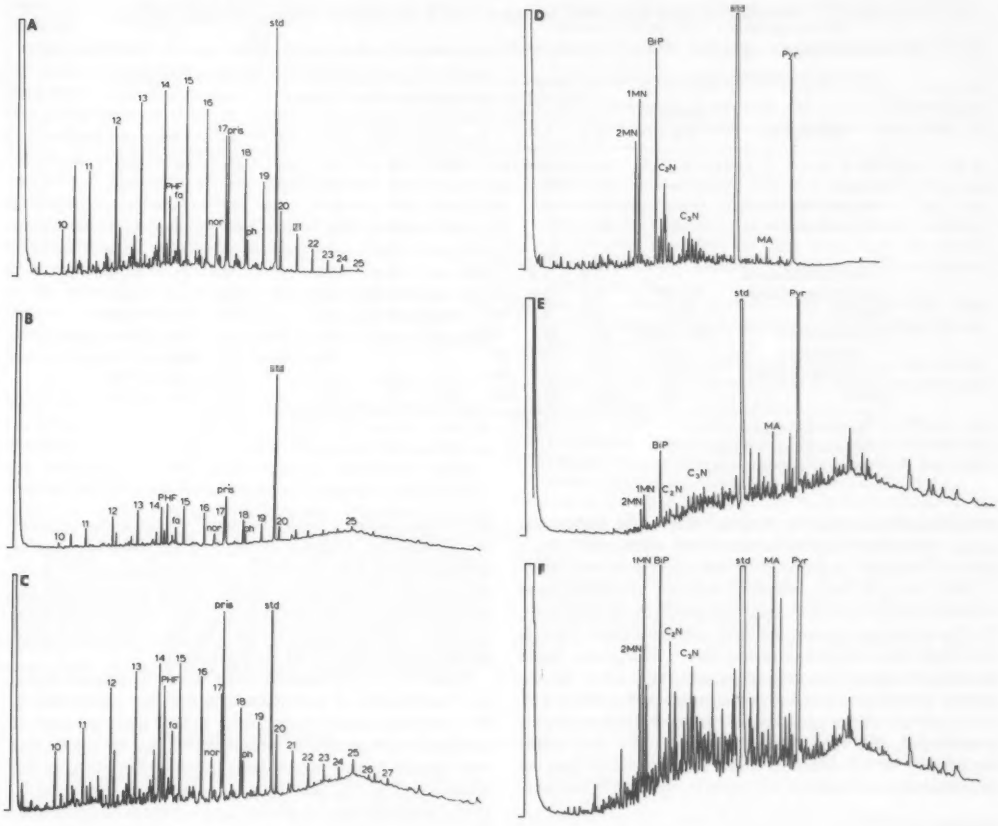

FIG. 4. Gas chromatograms of the F_1 and F_2 fractions extracted from microcosm samples. A and D, water from the experimental (storm) tank taken 6 h after the hydrocarbon addition; B and E, sediment from the storm tank, taken 4 d after the addition; C and F, sediment from the control tank, also taken 4 d into the experiment. In addition to the symbols explained in Fig. 1, PHF, BiP, MA, and Pyr indicate the positions of perhydrofluorene, biphenyl, 9-methylanthracene, and pyrene, respectively.

sibly the high levels of resuspended sediment changed the initial mechanism of sedimentation and brought about a more wholesale scavenging of hydrocarbons. Bacteria which were probably carried into the water column with the resuspended sediment appear not to have changed the relative removal rates to any noticeable extent, possibly because they were removed from their natural environment. The half lives of specific hydrocarbons in the microcosms have some variability from experiment to experiment ($\sim \pm 10$ h, Gearing and Gearing 1982a), so the differences noted between storm and control microcosms may be analytical artifacts. A comparison of the relative aqueous concentrations of individual compounds over time showed no gross differences (Fig. 3).

There were, however, significant differences between the hydrocarbon contents of particulate matter collected by sediment traps in the two microcosms. Total hydrocarbons associated with storm tank particles averaged 900 μg/g, whereas the control tank particles contained almost ten times as much, or 9000 μg/g. The latter value was quite similar to previously reported concentrations in MERL oil experiments (Gearing et al. 1980; Wade and Quinn 1980) and in the field following an oil spill (Boehm et al. 1980). The lower particulate hydrocarbon loading and thus lower partition ratio in the storm microcosm may have resulted from the lower sorptive capacity of silt and clay relative to organic detritus (Herbes 1977; Paris et al. 1978). Although the rapid mixing increased the mineral matter suspended in the water by a factor of 30, previous simulated storms in the microcosms have increased chlorophyll-*a* (a measure of plankton biomass) only by a factor of three or less. Another possibility is that the amount

TABLE 3. Percentage of added hydrocarbon calculated to be in the sediments (average of control and storm microcosms) over time, and behavior assuming exponential decay ($C = C_o e^{-kt}$, $t_{1/2} = \frac{\ln 2}{k}$).

Hydrocarbon	Solubility (μg/L)	Time (days) after addition to water column							C_o	$t_{1/2}$,d	r^2
		1 d	4 d	7 d	24 d	42 d	127 d	160 d			
ΣF_1	—	63	73	63	36	48	27	14	62	84	0.92
pristane	—	49	63	58	31	35	14	8.5	53	62	0.96
n-heptadecane	~1[a]	60	52	46	21	34	16	2.8	50	48	0.89
perhydrofluorene	—	54	73	75	39	40	20	15	61	78	0.95
ΣF_2	—	24	36	33	18	15	1.5	0	36	21	0.98
2-methylnaphthalene	—	2.8	1.8	7.2	0.8	0.4	0	—	3.3	13	0.78
1-methylnaphthalene	25 000[b]	2.0	1.6	13	0.6	0.05	0	0	4.4	6.6	0.85
biphenyl	7500[b]	5.0	5.1	14	2.0	0.35	0	—	8.4	9.2	0.90
C_2-naphthalenes	1300–8000[b]	10	11	9.6	2.6	1.9	0	0	10	16	0.86
C_3-naphthalenes	~2000[c]	21	24	19	6.0	7.0	0	0	20	24	0.74
9-methylanthracene	260[c]	45	65	56	30	10	4.6	1.6	48	33	0.96
pyrene	135[c]	48	51	140	25	22	10	9.0	54	56	0.84

[a]Sutton and Calder (1974).
[b]Eganhouse and Calder (1976).
[c]Mackay and Shiu (1977).

of hydrocarbons added was limiting, that is, the higher suspended particulate load in the storm tank represented only a mineral "dilution" of particles already present in both tanks.

Mass balances were attempted between hydrocarbons in sediment trap particles and cored sediments (see next section). For the storm microcosm, the total suspended particulate oil calculated from sediment trap data was ~ 62% of that found in sediment cores. The percentage was much lower for the control microcosm. It is known that traps preferentially collect larger and denser particles and that their efficiency varies considerably with water velocity (Gardner 1980). Due to this inefficiency of the sediment traps, all quantitative data on hydrocarbon sedimentation was based on material from cores.

SEDIMENTS

Simulation of storm conditions did not increase the sedimentation of oil in the MERL microcosms with the concentrations employed. The percentage of added petroleum hydrocarbons reaching the sediments was, on average, 6% lower in the storm tank than in the control. This difference is within the analytical and sampling variability of the measurement (Gearing et al. 1978; Wade and Quinn 1980). Figure 3 shows the amounts for three individual compounds and also illustrates the overlap between intertank and intratank variability. During the first week an average of 44% of the total oil added was found in the sediments of the storm tank, compared with 68% in the control. Biodegradation during this period removed some but not a great deal of the oil, as evidenced by the ratios of *n*-alkanes to isoprenoid hydrocarbons (Fig. 4B and C). In previous experiments in which No. 2 fuel oil was added over a period of months and the sedimentary hydrocarbons showed evidence of more extensive biodegradation, the maximum percentages of sedimented oil were 36 and 44% for two microcosms (Gearing et al. 1980).

These values reflect the oil found in the top 0–1 cm of sediment. As in previous experiments (Gearing et al. 1980), the oil was gradually carried deeper (2–3 cm) in the sediment by bioturbation. Analyses of the 1–2 cm depth sections of sediment in this experiment revealed a small amount of oil, on average 22% of that in the surface. Depth sections from the storm microcosm had almost exactly the same amount of oil as in the control, indicating that the storm had not caused greater preservation of oil by rapid burial.

There was also no apparent difference in the relative chemical distributions of petroleum hydrocarbons sedimented in the storm and control microcosms. In both tanks the suite of saturated hydrocarbons in the sediments (Fig. 4B and C) was very similar to that in the water column (Fig. 4A), in the dispersion (Fig. 1A), and in the original oil (see Gearing et al. 1980), although some degradation of *n*-alkanes had occurred. The suite of sedimented aromatics was similar in both tanks (Fig. 4E and F), and depleted in lower molecular weight compounds compared with the water column and dispersion (Fig. 4B and 1B). Such fractionation of oil during sedimentation has been noted in previous MERL experiments (Gearing et al. 1980) and laboratory studies (Meyers and Quinn 1973; Meyers and Oas 1978; Zurcher and Thuer 1978). In this experiment a more quantitative examination of chemical character and sedimentary behavior was made possible by (1) making a single addition of oil, (2) adding a suite of individual compounds covering a wider range of characteristics than No. 2 fuel oil, and (3) averaging the behavior from two microcosms.

Saturated hydrocarbons in the range studied (12–25 carbons) are all relatively insoluble, and more than 50% of each was rapidly carried to the sediments (Table 3). Sedimentary residence times varied in the order suggested by bacterial hydrocarbon degradation studies (e.g. Mechalas et al. 1973), cycloalkanes > isoprenoids > *n*-alkanes. Taken as a whole the No. 2 fuel oil saturates, which comprise ~ 80% chromatographically unresolved compounds, remained about as long as the spiked cycloalkane, perhydrofluorene. Assuming exponential decay, we calculated that it would require more

than a year for removal of 99% of this compound (half life of 78 d).

There was much more variability in the sedimentary behavior of the aromatic hydrocarbons examined (Table 3), which have aqueous solubilities spanning a much broader range than that of the saturates. With increasing molecular weight (and concomitant decreasing solubility) there was a steady increase in both the percentage of hydrocarbon reaching the sediment and its half life there. Within the naphthalene series, each additional substituent carbon atom increased the amount transported to the bottom by 100−150% and the sedimentary residence time by ~ 50%. Higher molecular weight aromatics (9-methylanthracene, pyrene) were similar to the saturates in the proportions sedimented, although their sedimentary removal rates were somewhat faster. Such measurements of sedimentation and persistence could eventually make possible semiquantitative estimates for actual spills.

Overall, the presence of high levels of turbulence and resuspended particulate matter (storm conditions) had little or no effect on the removal of oil (330−500 μg/L) from a simulated estuarine water column. Much more important to the sedimentation and preservation of petroleum hydrocarbons was their individual chemical character. Fifty to 60% of the less soluble hydrocarbons (aromatics with three or more rings and saturates with 10 or more carbon atoms) were rapidly transported to the sediments of both storm and control microcosms, where their half lives ranged from 33 to 80 d (methylanthracene to cycloalkanes, respectively). Much less of the more soluble, two-ring aromatics was transported to the bottom (3−20%), and the amounts sedimented and residence times there increased with increasing aliphatic substitution.

Acknowledgments

This research was funded by U.S. Environmental Protection Agency cooperative agreement No. CR807795 with the University of Rhode Island. Dr Candace Oviatt was of great help in the design of the experiment. Dr James Quinn read and improved the paper before its submission.

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Humic Acids Reduce Bioaccumulation of Some Polycyclic Aromatic Hydrocarbons[1]

G. J. LEVERSEE[2], P. F. LANDRUM[3], J. P. GIESY[4], AND T. FANNIN[5]

Savannah River Ecology Laboratory Drawer E, Aiken, SC 29801, USA

LEVERSEE, G. J., P. F. LANDRUM, J. P. GIESY, AND T. FANNIN. 1983. Humic acids reduce bioaccumulation of some polycyclic aromatic hydrocarbons. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 63–69.

In laboratory studies, *Daphnia magna* were exposed for 6 h to five polycyclic aromatic hydrocarbons (PAH) (0.1–2.0 μg/L) in water with and without Aldrich® humics (2 mg DOC/L). Compared to results in nonhumic water, accumulation of PAH by *Daphnia* in water with humics was significantly reduced for benzo[*a*]pyrene (−25%) while it was increased for methylcholanthrene (+210%). Humics did not significantly alter *Daphnia* accumulation of anthracene, dibenzanthracene or dimethylbenzanthracene. In additional studies, humics reduced *Daphnia* accumulation of benzo[*a*]pyrene (B[*a*]P) over a range of B[*a*]P concentrations (1.1–5.4 μg/L) exceeding the reported limit for water solubility (1.1–1.2 μg/L). Humics consistently increased *Daphnia* accumulation of methylcholanthrene (MC) over a range of humic concentrations from 0.2 to 10.0 μg DOC/L. Particulates and DOC (10–12 mg TOC/L) occurring naturally in two South Carolina streams reduced *Daphnia* accumulation of B[*a*]P by 38–66%, with about 40% of the overall reduction attributable to DOC. We conclude that dissolved refractory organics may significantly affect bioavailability and environmental transport of some PAH in fresh waters.

LEVERSEE, G. J., P. F. LANDRUM, J. P. GIESY, AND T. FANNIN. 1983. Humic acids reduce bioaccumulation of some polycyclic aromatic hydrocarbons. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 63–69.

Dans des études de laboratoire, des *Daphnia magna* ont été exposées pendant 6 h à cinq hydrocarbures aromatiques polycycliques (HAP) (0,1–2,0 μg/L) dans de l'eau contenant ou non des dérivés humiques Aldrich® (2 mg COD/L). Comparativement à ce qui se produit dans une eau non humique, l'accumulation de HAP par *Daphnia* dans de l'eau contenant des dérivés humiques est nettement réduite en ce qui a trait au benzo[*a*]pyrène (−25 %), tandis qu'elle est plus élevée dans le cas du méthylcholanthrène (+210 %). Les dérivés humiques ne modifient pas pour la peine l'accumulation de l'anthracène, du dibenzanthracène ou du diméthylbenzanthracène. Dans des études supplémentaires, les dérivés humiques ont réduit l'accumulation du benzo[*a*]pyrène (B[*a*]P) dans une gamme de concentration (1,1–5,4 μg/L) dépassant la limite connue de solubilité dans l'eau (1,1–1,2 μg/L). Les dérivés humiques causent une plus forte accumulation par *Daphnia* du méthylcholanthrène (MC) sur une gamme de concentration humique de 0,2–10,0 μg COD/L). Les matières particulaires et le COD (10–12 mg COD/L) présents naturellement dans deux cours d'eau de la Caroline du Sud réduisent d'environ 38–66 % l'accumulation de B[*a*]P par *Daphnia*, 40 % de la réduction globale étant attribuables au COD. Nous concluons que des substances organiques réfractaires dissoutes peuvent influer de façon significative sur l'accessibilité aux organismes et le transport dans l'environnement de certains HAP présents en eaux douces.

Received March 18, 1982
Accepted October 12, 1982

Reçu le 18 mars 1982
Accepté le 12 octobre 1982

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Keene State College, Keene, NH 03431, USA.
[3]Present address: Great Lakes Environmental Research Lab, NOAA, Ann Arbor, MI 48104, USA.
[4]Present address: Pesticide Research Center, Michigan State University, East Lansing, MI 48824, USA.
[5]Present address: Wyoming Game and Fish Lab, Lander, WY 82540, USA.

Printed in Canada (J6847)
Imprimé au Canada (J6847)

EVIDENCE suggests that the most important pathway of bioaccumulation of polycyclic aromatic hydrocarbons (PAH) is direct uptake from water by simple partitioning into lipids (Neely et al. 1974). It has been demonstrated that humics in freshwater systems may form stable complexes affecting the transport of trace organic compounds including dialkyl phthalates (Ogner and Schnitzer 1970), pesticides (Wershaw et al. 1969), amino acids (Lytle and Perdue 1981), and cholesterol (Hassett and Anderson 1979). In marine systems, dissolved organic matter (DOM) reportedly increased the solubility of *n*-alkanes (Boehm and Quinn 1974) and decreased the uptake of aromatic and other petroleum hydrocarbons by the bivalve *Mercenaria mercenaria* (Boehm and Quinn 1976). It is generally believed that DOM in rivers is precipitated on exposure to seawater and deposited in estuarine and nearshore marine sediments (Gardner and Menzel 1974). The potential for deposition of PAH associated with DOM precipitated in estuarine sediments may account for some presently unknown fraction of organic trace contaminants found in estuarine sediments.

It is therefore of interest to determine the effects of freshwater humic and fulvic acids on PAH environmental transport. Of particular interest are the effects of humics on direct uptake of PAH by freshwater biota. Studies on humics as they affect PAH accumulation in *D. magna* were conducted to determine (1) if a "standard" humic acid (Aldrich®) at one concentration (2 mg DOC/L) affected the bioaccumulation of several PAH, (2) if observed effects in some PAH varied predictably with humic concentration, (3) if observed effects changed over a range of PAH concentrations, some of which exceeded limits of water solubility, and (4) if humics in natural waters behaved similarly.

Materials and Methods

Six radiolabeled PAH were studied: naphthalene, anthracene, benzo[*a*]pyrene, dibenzanthracene, dimethylbenzo-[*a*]anthracene, and methylcholanthrene (Table 1). PAH were selected to provide a broad range of molecular weights, water solubilities, octanol–water partition coefficients, structural configurations, and substitutions. Stocks of PAH were diluted in solvents as shipped and added to test water in volumes of 1–30 μL/L. The ^{3}H-dibenzanthracene specific activity was adjusted to 38 GBq/mmole by addition of unlabeled dibenzanthracene (Aldrich®, 97% pure) to water at the time of labeling. Water was labeled in bulk (1–4 L) and thoroughly shaken for several minutes before use. All preparative, analytical, and experimental procedures were carried out under gold fluorescent light ($\lambda \geq 500$ nm) to minimize photodegradation of PAH.

For benzo[*a*]pyrene, experimental water was analyzed after 6 h to insure that *Daphnia* were being exposed primarily to parent compound and not to B[*a*]P degradation products. Triplicate 200-mL aliquots were acidified to pH 4 with glacial acetic acid. Each aliquot was extracted three times with 50-mL volumes of benzene and then three times with 50-mL volumes of ethyl acetate. All benzene and ethyl acetate extracts were combined (total volume ≃ 300 mL) and dried by passing through anhydrous Na_2SO_4. The water-free extracts of each aliquot were sampled in triplicate (3 × 0.5 mL) to determine total radioactivity. Extracts were then reduced in volume to ≃ 100 μL by rotary flash evaporation and evaporation under a nitrogen stream. Extracts were spotted on Merck® silica gel thin-layer chromatography plates. Plates were developed in 9:1 (v/v) hexane:benzene, and spots were visualized using ultraviolet light. B[*a*]P was identified using co-chromatography of authentic standards. Plates were scraped and counted using a Beckman LS8100 liquid scintillation counter. Degradation products were identified as non-B[*a*]P^{14}C.

Test water was prepared by adding inorganic salts to Milli-Q® deionized water as follows (all concentrations mg/L): $NaHCO_3$ = 48, $CaSO_4 \cdot 2H_2O$ = 30, $MgSO_4$ = 30, KCl = 2. With these inorganic additions, water quality was as follows: pH 7, hardness 20 mg/L as $CaCO_3$, alkalinity 120 mg/L as $CaCO_3$, conductivity 130 μS/cm.

A humic stock solution was prepared from Aldrich® humic acid (H-1675-2, Lot #082091) by repeating the following steps three times. Humic acid was dissolved in 0.1 mol NaOH/L. The crude solution was centrifuged at 13 000 × *g* for 30 min. The pH was adjusted to 2 with 6.0 mol HCl/L and the solution allowed to stand for 18 h. Humic acid precipitate was collected by centrifugation (4000 × *g* for 20 min). The final humic solution was adjusted to pH 7 and dialyzed repeatedly against deionized water until conductivity was < 10 μS/cm. Stock humics were added to labeled test water to a final, nominal concentration of 2.0 mg/L dissolved organic carbon (DOC) unless otherwise noted. Blanks of Milli-Q® water were < 0.1 mg/L, and hardened Milli-Q® water < 0.2 mg/L. Total carbon and inorganic carbon in freshwater were determined using a Beckman Model 915B Carbon Analyzer and DOC was calculated by difference.

PAH BIOAVAILABILITY

Daphnia magna from laboratory cultures (Southeastern Research Laboratory. U.S. EPA, Athens, GA) were exposed for 6 h to PAH in paired 1-L beakers with and without humics (60–70 *Daphnia*). Five samples of 10 animals were removed by pipet from each test water, collected on nylon netting, rinsed quickly in 50 mL deionized water, and poured through a Millipore® filter apparatus. Animals were collected on tared 25 mm Millipore® Type HA cellulose acetate filters, dried over desiccant for 24–48 h and sample dry weights were determined on a Cahn Model 4700 Electrobalance. Animals and filters were combusted in a Packard Model 306 sample oxidizer, CO_2 and H_2O collected in suitable trapping agents, and counted by liquid scintillation. Samples were corrected for quench using internal and external standards and the sample channels ratio method. In B[*a*]P studies, *Daphnia* were analyzed for B[*a*]P and transformation products (non-B[*a*]P^{14}C) to insure that accumulation was primarily of parent compound (Leversee et al. 1981).

To evaluate the importance of natural particulates and DOC on B[*a*]P bioavailability, similar experiments were conducted using water from Upper Three Runs Creek (UTRC) and Skinface Pond on the Department of Energy's Savannah River Plant, near Aiken, SC. B[*a*]P uptake was determined in water directly from the creek, in water filtered to remove particles (0.45-μm Whatman GFC glass fiber filters, precombusted at

TABLE 1. Radio-labeled PAH used in bioavailability studies.

Compound	Label	Specific activity (GBq/mmol)	Solvent	Radiopurity (%)	Source
Naphthalene mw 128	1-^{14}C	0.325	Ether	≥98	California Bionuclear lot 2545
Anthracene mw 178	9-^{14}C	0.122	Acetone	≥98	California Bionuclear lot 770824
Benzo[*a*]pyrene mw 252	7,10-^{14}C	0.803	Toluene	≥98	Amersham Batch 29
1,2,5,6-Dibenzanthracene mw 278	^{3}H(G)	1121.1	Benzene	≥97	New England Nuclear lot 1253-021
7,12-dimethyl Benzo[*a*]anthracene mw 256	dimethyl^{14}C	3.589	Benzene	≥98	New England Nuclear lot 1267-176
3-Methylcholanthrene mw 268	6-^{14}C	2.109	Benzene: ethanol (9:1)	≥98	New England Nuclear lot 1231-171

TABLE 2. Effect of Aldrich® humic acids (2 mg DOC/L) on accumulation of five PAH by *Daphnia magna*.

Initial water PAH concentration (μg/L)	Humic concentration DOC (mg/L)	Bioaccumulation[a] (6 h)	Bioconcentration[b] factor (6 h)
Anthracene (1.96)	0.2	82.3 (19.7)[c]	607
mw 178	2.0	43.9 (4.0)	319
Benzo[*a*]pyrene (1.15)	0.2	131.6 (7.3)[d]	2745
mw 252	2.0	99.4 (7.7)	2158
Dimethylbenzanthracene (1.57)	0.2	64.2 (23.2)	968
mw 256	2.0	55.8 (30.0)	666
Methylcholanthrene (1.29)	0.2	34.0 (7.4)[d]	667
mw 268	2.0	105.5 (10.8)	2064
Dibenzanthracene (0.72)	0.2	20.3 (0.8)	652
mw 278	2.0	24.2 (2.4)	773

[a]Bioaccumulation: nmol/g dry wt *Daphnia*. Dry/wet = 0.06. Mean dry weight for a single sample of 10 *D. magna* = 1.14 mg.

[b]Bioconcentration factor: $\frac{\text{ng PAH/g wet wt } \textit{Daphnia}}{\text{ng PAH/mL water}}$.

Calculated using final water concentrations.

[c]$\bar{x}$ (SE), $n = 5$.

[d]$P < 0.05$ (t test).

550°C, 8 h), and in filtered water UV photo-oxidized to remove DOC. DOC in 100-mL aliquots of water was removed by exposure for 6 h in a La Jolla Scientific UV Photo-oxidizer with a few drops of hydrogen peroxide as a catalyst. Oxidized water was filtered to remove colloidal iron, hardened by the addition of salts and refiltered before use.

Results and Discussion

Concentrations of five PAH were determined in *Daphnia magna* after 6-h exposures in water with Aldrich® humics (DOC = 2.0 mg/L) and in water without humics (DOC ≤ 0.2 mg/L). *Daphnia* in humic waters had significantly lower concentrations of benzo[*a*]pyrene (B[*a*]P) (−24.5%) than comparable animals in nonhumic waters (Table 2). On the other hand, humics increased concentrations of methylcholanthrene (MC) in *Daphnia* (+210%). Humics had little effect on dimethylbenzanthracene (DMBA) (−13.1%) or dibenzanthracene (DBA) (+19.1%). While the effect on anthracene (−46.7%) appeared large, it was not significant due to large sample variance. Results reported assume that all radioactivity was parent compound (see below). These results are significant for two reasons: (1) they demonstrate that humics at low concentrations affect bioaccumulation of some PAH; (2) they demonstrate that humics may either increase or decrease bioaccumulation. Mechanisms which may be operating to cause these differences will be considered later, but several questions concerning the relationship between 6 h

TABLE 3. Effect of Aldrich® humic acids on PAH accumulation in *Daphnia magna*. Results (ANOVA) were highly significant for B[*a*]P, not quite significant at $P < 0.05$ for anthracene, and not significant for naphthalene.

PAH	Humic concentration (DOC in mg/L)	Bioaccumulation[a] (6 h)	Bioconcentration[b] factor
Benzo[*a*]pyrene[c]	0.3	139.2 (14.2)	1716
mw 252	1.5	90.9 (7.6)	979
	5.7	72.6 (5.7)	838
		$F_{2,12}=12.19$ ($P < 0.005$)	
Anthracene	0.3	37.2 (2.0)	389
mw 178	1.5	34.9 (2.0)	362
	5.7	31.0 (1.1)	340
		$F_{2,12}=3.16$ (NS)	
Naphthalene	0.3	1.7 (0.2)	61
mw 128	1.5	1.6 (0.3)	74
	5.7	1.8 (0.1)	57
		$F_{2,6}=0.95$ (NS)	

[a]Bioaccumulation: nmoles PAH/g dry wt *Daphnia*. Mean ± SE, $n = 5$. Naphthalene $n = 3$.

[b]Bioconcentration factor: $\frac{\text{ng PAH/g wet wt } Daphnia}{\text{ng PAH/mL water}}$.

[c]Initial B[*a*]P water concentration was 1.5 µg/L (6.0 nmol); Anthracene was 1.3 µg/L (7.2 nmol); Naphthalene was 0.8 µg/L (6.6 nmol).

TABLE 4. Effect of Aldrich® humic acids on methylcholanthracene accumulation by *D. magna*.

Humic concentration (DOC mg/L)	Bioaccumulation[a] (6 h)	Bioconcentration factor[b] (6 h)
0	142.1(15.2)[c]	$\frac{2401}{3.1} = 775$
2.0	309.3(66.1)	$\frac{5288}{2.9} = 1823$
4.0	311.2(47.1)	$\frac{5260}{2.8} = 1879$
6.0	376.9(71.6)	$\frac{6370}{2.9} = 2197$
8.0	260.1(40.8)	$\frac{4396}{3.0} = 1465$
10.0	233.6(12.5)	$\frac{3945}{3.6} = 1096$

[a]Bioaccumulation: nmol methylcholanthrene/g dry weight *D. magna*.

[b]Bioconcentration factor: $\frac{\text{ng methylcholanthrene/g wet weight } D.\ magna}{\text{ng methylcholanthrene/mL water}}$.

[c]$\bar{x}$ (SE), $n = 5$.

[d]Water methylcholanthrene concentration at 6 h used for BCF. Initial mean water concentration was 3.5 (0.04) µg/L.

uptake and steady state bioconcentration of unaltered PAH must be addressed.

Evidence from this and other studies suggests that results reported for the 6 h uptake tests were not transient differences but were representative of steady state differences for all PAH tested. In preliminary 24-h uptake studies, steady state radioactivity in *D. magna* was reached within 6 h for anthracene, and B[*a*]P. Approximately 60–80% of steady state was reached after 6 h with DMBA, DBA and MC. In no case did the relative difference between *Daphnia* PAH in humic and nonhumic waters change after 6 h. In *Daphnia pulex*, Southworth et al. (1978) reported that 6-h exposures produced steady state concentrations of naphthalene and anthracene, while up to 24 h were required for benzanthracene, results consistent with our observations. The values reported do not necessarily represent maximum bioaccumulation, since depletion of water PAH concentrations can occur in static tests. It will be noted that results for *Daphnia* accumulation of anthracene and methylcholanthrene are not identical in Tables 2, 3, and 4 at comparable humic concentrations. These differences are due to different initial concentrations of PAH, as well as to inherent variance due to individual experimental procedures over several months. Trends within replicate experiments have always been consistent. Previous studies have shown that *Daphnia* have slow PAH biotransformation rates relative to accumulation rates (Herbes and Risi 1978; Leversee et al. 1981). In this study with ^{14}C–B[*a*]P, after 6 h, parent compound represented 91.3 ± 2.1% of test water activity and 92.8 ± 0.8% of *D. magna* activity, respectively. Biotransformation may be even less than 10% since some degradation of B[*a*]P on TLC plates has been observed (by P. F. Landrum). Active biotransformation and excretion of PAH reported for some invertebrates and fish are probably not important factors in PAH accumulation by *D. magna*.

The effect of varying Aldrich® humic acid concentrations (0.3–5.7 mg DOC/L) on accumulation by *Daphnia* of B[*a*]P, anthracene, and naphthalene was determined. Humics significantly reduced the accumulation of B[*a*]P but results were not significant for anthracene and naphthalene (Table 3). In this simple unsubstituted PAH series, the effect of humics was greatest for B[*a*]P > anthracene > naphthalene, which is consistent with the order of reported octanol–water partition coefficients. This suggests that hydrophobic PAH may be partitioned competitively between *Daphnia* lipids and humics. Although the effect of humics on B[*a*]P and anthracene

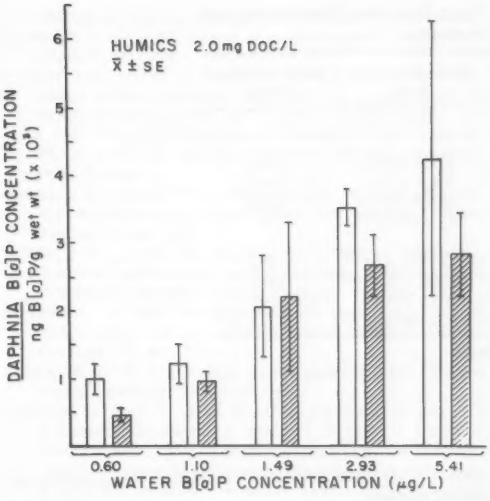

FIG. 1. Effect of Aldrich® humic acids (2.0 mg DOC/L) on *Daphnia magna* accumulation of B[*a*]P at five B[*a*]P concentrations. Shaded bars represent water with humics, open bars water without humics.

was greatest at highest humic concentrations, there was not a simple linear relation between humic concentration and *Daphnia* PAH concentration. The greatest effect was found between no humic acids and 1–2 mg DOC/L. Additional data at several concentrations of PAH and humics will be necessary before determining the possibility that predictive sorption isotherms can be developed for PAH like B[*a*]P.

The effect of varying humic concentrations over a wide range (0–10 mg DOC/L) while holding initial PAH concentration constant was determined using methylcholanthrene (3.5 μg/L). At all humic concentrations, *Daphnia* accumulated significantly more MC than animals in nonhumic water (Table 4). Among various humic concentrations (2–10 mg DOC/L), there were no significant differences in *Daphnia* MC concentration. The lack of a simple predictive relation between humic concentration and *Daphnia* PAH concentration was apparent for MC, as it was for anthracene and B[*a*]P.

The effect of varying PAH concentration (B[*a*]P = 0.6–5.4 μg/L) while holding humic concentration constant (2.0 mg DOC/L) was also examined. In general, results confirmed our previous conclusions that humics reduced B[*a*]P accumulation in *Daphnia* (Fig. 1). The large variance inherent in working with small samples of *Daphnia* and PAH concentrations of 1–10 μg/L resulted in a significant difference between *Daphnia* in humic and nonhumic waters only at 2.9 μg B[*a*]P/L (*t*-test, $P < 0.05$) (Fig. 1). It has been suggested that marine DOM increased uptake of the aromatic fraction of No. 2 fuel oil by *Mercenaria mercenaria* at high aromatic concentrations by a process of co-solubilization (Boehm and Quinn 1976). This study suggests that no apparent major difference in the effects of humics occurred when B[*a*]P concentration exceeded the reported limits of B[*a*]P water solubility (1.1–1.2 μg/L). Also, it did not appear that increasing B[*a*]P concentrations in the range examined saturated the humic effect. The mean values for *Daphnia* B[*a*]P concentrations were still reduced in the presence of humics, even at initial B[*a*]P concentrations in water of 2.9 and 5.4 μg/L.

The effect of natural organics and particles on *Daphnia* B[*a*]P accumulation was examined to determine whether results would be comparable to those with Aldrich® humics. Upper Three Runs Creek and Skinface Pond, typical coastal plain surface waters, are soft (hardness ≃ 10) mg/L as $CaCO_3$) acidic (pH 6.1) and rich in humic and fulvic acids (10–12 mg TOC/L). In both waters, *Daphnia* B[*a*]P concentrations were significantly reduced by the presence of particles and DOC (Table 5). Removal of particles and dissolved organics from Skinface Pond water caused a threefold increase in *Daphnia* B[*a*]P concentrations, while in Upper Three Runs Creek water, a 60% increase occurred. Dissolved organics caused about 40% of the observed effect in both waters, i.e. particles and DOC were about of equal importance. In addition to direct effects, dissolved refractory organics are important in formation of organic films on clay particles (Hunter 1980). Over 90% of DOC in Skinface Pond and Upper Three Runs Creek waters is in small ultrafilter size fraction $0.0015 \leq F \leq 0.0009$ μm (nominal mw < 500) (Giesy and Briese 1978) and the effect observed may be due to this fraction. The humic acids of these waters have been well characterized in terms of seasonal changes in DOC concentration, molecular size fractions and effects on metal speciation, metal binding, and metal toxicity (Giesy and Briese 1978; Giesy et al. 1982).

In summary, results of these *Daphnia* PAH uptake studies suggest a complex effect of humic acids on PAH bioavailability. In general, humics reduce the partitioning into *Daphnia* of single unsubstituted PAH, with the greatest reduction observed in PAH having the largest octanol–water partition coefficient (e.g. B[*a*]P > anthracene > naphthalene). Methylcholanthrene accumulation by *Daphnia* was increased by humics in a manner which is not clear. This apparent anomaly was found in many replicate studies in our laboratory but should be confirmed by other workers. If correct, this unexpected result could have significant implications for models of PAH bioaccumulation.

In the test system used, significant interactions may occur among any or all components (PAH–humics–*Daphnia*). Partitioning into internal lipids is usually assumed, but Crosby and Tucker (1971) found that up to 50% of DDT in *Daphnia magna* was on the carapace, probably by simple surface sorption. Little is known concerning humic–organism interactions. Other studies in our laboratory have demonstrated that humics reduce B[*a*]P uptake in both bluegill sunfish (*Lepomis machrochirus*) and chironomid larvae (*Chironomus riparius*). Thus we feel that the results observed are not unique to *Daphnia* and probably do involve significant humic–PAH interactions. Questions concerning the nature of these interactions are better answered using chemical techniques such as affinity or gel permeation chromatography, ultrafiltration, or solvent extraction. Our purpose was to demonstrate effects of humics on bioaccumulation using a range of PAH.

TABLE 5. Effect of Skinface Pond and Upper Three Runs Creek organics and particles on B[*a*]P accumulation by *Daphnia magna*.

Water source and treatment	Organic carbon (mg/L)	Bioaccumulation[a] (6 h)	Bioconcentration[b] factor
Upper Three Runs Creek			
Untreated	10.0	227.4 (12.0)	2571
Filtered (0.45 μm)	5.5	304.4 (7.1)	3581
Filtered-oxidized	0.2	367.2 (13.9)	4656
		$F_{2,12}$=37.87[c]	
Skinface Pond			
Untreated	12.1	70.4 (2.6)	903
Filtered (0.45 μm)	—	156.2 (5.6)	2312
Filtered-oxidized	0.2	206.7 (13.1)	3292
		$F_{2,12}$=67.84[c]	

[a] $\bar{x}$ (SE), $n = 5$. Values = nmol/g dry weight.

[b] $\frac{\text{ng B[}a\text{]P/g wet weight } \textit{Daphnia}}{\text{ng B[}a\text{]P/mL water}}$.

[c] ANOVA, $P < 0.001$.

Most models for humic interactions with both metals and trace organics assume covalent or other binding to humics (Parris 1980) which competes for binding to biota. It has been suggested, however, that natural organics may increase or decrease bioavailability and biological effects of metals depending on organic molecular size class, number and type of binding sites and conditional stability constants (Giesy et al. 1977; Giesy et al. 1982). The same may be true of humic complexed PAH. Natural organic matter in river water reportedly binds cholesterol, reducing efficiency of solvent extraction. Gel permeation studies suggest that the cholesterol is bound to high molecular weight organics (Hassett and Anderson 1979). Whatever the nature of the effect observed (increased or decreased bioavailability), studies with B[*a*]P and MC suggest that it is reasonably consistent over a range of both humic and PAH concentrations. However, the results reported here suggest that a simple linear relation between humic concentration and PAH bioconcentration does not exist. Additional data are needed over a wider range of humic concentrations and different humic types.

DOC is the most abundant form of reduced carbon in freshwater (Hobbie and Likens 1973; Wetzel and Manny 1977; Naiman and Sibert 1978; Rich and Wetzel 1978), estuaries (Head 1976), and oceans (Williams 1975). Given an average river organic carbon concentration of 10 mg C/L, the annual input to oceans can be calculated at 3×10^{14} g C (Handa 1977), of which 60–90% is DOC (Dahm 1981). Estimates of labile organics (amino acids, lipids, etc.) in river systems vary widely but are in the range of 20–40% of DOC (Larsen 1978), the remainder being refractory humic and fulvic acids.

Over 230 000 t of PAH enter the oceans and surface waters of the world each year (Suess 1976). A significant portion of that is from industrial and urban runoff. These amounts can be expected to increase due to increased coal use through direct combustion, or from processing into synfuels (Gehrs 1976) and from petroleum spills. Formation of PAH–humic complexes may alter partitioning of PAH into biota and organic sediments and thereby alter downstream transport. An understanding of the factors affecting this transport will be important in developing models for PAH input into estuarine and marine systems.

Acknowledgments

Thanks to Garfield Keaton, John Bowling, Sarah Gerould, and Pam Tolbert for technical assistance in various aspects of this study. Dr James Alberts materially assisted this study through many long discussions and critical comments. This research was supported by Interagency Agreement EPA-78-D-X0290 between the U.S. Environmental Protection Agency and U.S. Department of Energy and Contract DE-AC09-76SR00819 between the U.S. Department of Energy and the University of Georgia.

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Natural Weathering of Oil in Marine Sediments: Tissue Contamination and Growth of the Littleneck Clam, *Protothaca staminea*[1]

J. W. ANDERSON

Battelle, Marine Research Laboratory, 439 West Sequim Bay Road, Sequim, WA 98382, USA

R. G. RILEY

Pacific Northwest Laboratory, Richland, WA 99352, USA

S. L. KIESSER

Battelle, Marine Research Laboratory, 439 West Sequim Bay Road, Sequim, WA 98382, USA

B. L. THOMAS

Pacific Northwest Laboratory, Richland, WA 99352, USA

AND G. W. FELLINGHAM

Battelle, Marine Research Laboratory, 439 West Sequim Bay Road, Sequim, WA 98382, USA

ANDERSON, J. W., R. G. RILEY, S. L. KIESSER, B. L. THOMAS, AND G. W. FELLINGHAM. 1983. Natural weathering of oil in marine sediments: tissue contamination and growth of the littleneck clam, *Protothaca staminea*. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 70–77.

Three groups (90 per group) of small (<30 mm) littleneck clams, *Protothaca staminea*, were placed in the intertidal environment of Sequim Bay, Washington for 1 yr to measure the effects of oiled sediment on growth and tissue contamination. Detailed glass capillary gas chromatographic analyses of initial and final sediment samples and tissues were used to describe the fate of specific oil components in the sediment, with depth, and the uptake by the clams. Concentrations of oil in sediments receiving a top layer (3 cm) of highly contaminated sediment reached background levels after 1 yr, while sediment mixed to depth (10 cm) with oil still contained measurable contamination at the 5–10 cm depth. The pattern of specific hydrocarbon loss is in agreement with results of spill studies, molecular weight relationships, and biodegradation data. The ratios of tissue concentrations to final sediment concentrations for phenanthrenes, alkylnaphthalenes, and dibenzothiophenes were all between 0.16 and 0.18. This suggests that the sulfur-containing compounds were not preferentially retained in tissues. Statistical analyses of 31–48 individually measured and marked clams (per group) showed that growth in oil-treated sediment was significantly ($P < 0.001$) slower than in clean sediment. In addition, oil mixed into sediment (10 cm) produced greater tissue contamination and more reduction in growth ($P < 0.01$) than a layer (3 cm) of oiled sediment.

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Trois groupes (90 par groupe) de petits clams (<30 mm), *Protothaca staminea*, ont été placés pendant un an dans un milieu intertidal de la baie de Sequim, dans l'État de Washington, en vue de mesurer les effets, sur la croissance et la contamination des tissus, d'un sédiment huileux. Nous avons effectué des analyses détaillées par chromatographie en phase gazeuse sur capillaire en verre d'échantillons de sédiment avant et après contamination, et avons utilisé les tissus pour décrire le sort de composants pétroliers spécifiques dans le

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6848)
Imprimé au Canada (J6848)

sédiment en fonction de la profondeur et leur assimilation par les clams. Les concentrations de pétrole dans le sédiment recevant une couche superficielle (3 cm) de matériel fortement contaminé atteignent des niveaux de base après un an, tandis que le sédiment mélangé à une profondeur de 10 cm avec du pétrole contient encore des quantités mesurables de contaminants à des profondeurs de 5−10 cm. Les modalités de perte d'hydrocarbures particuliers s'accordent avec les résultats d'études de déversements accidentels, les relations de poids moléculaire et les données de biodégradation. Les rapports entre concentrations tissulaires et concentrations finales dans le sédiment en ce qui a trait aux phénanthrènes, alkylnaphthalènes et dibenzothiophènes sont tous compris entre 0,16 et 0,18. Ceci donne à croire que les composés sulfurés ne sont pas retenus de manière préférentielle dans les tissus. Des analyses statistiques de 31−48 clams mesurés et marqués individuellement (par groupes) démontrent que la croissance dans un sédiment traité au pétrole est nettement ($P < 0{,}001$) plus lente que dans un sédiment propre. En outre, un pétrole mélangé au sédiment (10 cm) cause une plus forte contamination tissulaire et un ralentissement plus prononcé de la croissance ($P < 0{,}01$) qu'une couche (3 cm) de sédiment huileux.

Received March 18, 1982
Accepted October 4, 1982

Reçu le 18 mars, 1982
Accepté le 18 octobre 1982

BECAUSE bivalve mollusks, such as clams and oysters, are commercially valuable species that are also efficient accumulators of a wide range of toxicants, there are numerous publications regarding the uptake and effects of pollutants on these organisms. Many of the studies (reviewed by Malins 1977; Neff 1979; and Neff and Anderson 1981) concern the accumulation of hydrocarbons from water, the release rates in clean water and the associated effects on metabolic measurements. Research has generally involved laboratory exposures to water extracts of oil (water soluble fractions, WSF) or mechanically dispersed oil (oil in water dispersions, OWD). In some cases bivalves have been exposed in the laboratory to specific hydrocarbons dissolved in water, or to suspended particles coated with oil. Other studies have been conducted as part of field investigations after oil spills or in discharge areas. Many different biological and chemical approaches have been used in past studies to determine the degree of impact on the organisms and the retention time of petroleum components in the tissues.

Studies that utilized animals collected from accidentally or experimentally contaminated environments have often suffered from difficulties in interpreting (1) the state of health of the bivalves, (2) the significance of an abnormal response in the population, and (3) the relationship between observed impact and the concentration or characteristics of the contaminant. To determine the significance of much of the previous data, we felt it was very important to design a field experiment which combined detailed chemical data with a meaningful biological measurement of stress. In the Pacific Northwest, there are extensive shellfish beds containing large populations of littleneck clams (*Protothaca staminea*), as well as other commercially important species. Spilled oil might impact these intertidal beds, during calm or stormy weather, producing either surface oiling or sediments mixed to some depth with oil. This paper describes the changes in hydrocarbon component composition in these two situations over 1 yr and the resulting impact on the contamination and growth of small *P. staminea*.

Materials and Methods

Treatment of Animals and Sediments

In October of 1980 at low tide, approximately 300 clams (*P. staminea*) less than 30 mm in length, and several buckets of the surrounding coarse sand sediment were collected from Travis Spit, in Sequim Bay, Washington. The sediment was placed on a water table and held at ambient temperature (about 10°C) for 2 d. During this period, 270 clams were individually measured (length in mm) and marked with a small hand-held grinding tool (Moto-tool). As marking of the clams was being completed, two different oil treatments of the sediments were conducted. Since an earlier study (Anderson et al. 1978) had shown that surface sediments release oil more rapidly than deeper sediments, the layered treatment received a higher level of initial oil than the mixed treatment. For the mixed treatment, about 81 kg of sediment was mixed for an hour in a cement mixer with 163 g of Prudhoe Bay crude oil and about 2 L of seawater to produce a calculated concentration of about 2000 μg/g total oil in sediment. After mixing, the oiled substrate was placed in three fiberglass trays (48 × 28 × 12 cm deep), which contained two equally spaced partitions (16 cm apart) and a fiberglass screen cemented over openings in the bottom. The excess fluid containing some oil and soluble components was allowed to drain from these trays through the mesh bottoms. For the second (layered) treatment, substrate (23 kg) was mixed with 182 g of oil and about 600 mL seawater to produce a calculated concentration of 8000 μg/g total oil in sediment. Once prepared, this material was placed in a tray for drainage and transport to the field. Three other trays, which would eventually receive a 3 cm layer of this highly contaminated sediment, were filled to about 7 cm depth with clean substrate. As a control for the two oil treatments, clean sediment was placed into the final three sediment trays.

At high tide, 1½ d after the original collection, the 10 sediment trays were transported by boat to the installation site and

lowered by line to the bottom. At the evening low tide, about 8 h later, nine trays were placed into the beach, flush with the surrounding substrate. Ten small clams were placed into each section (28 × 16 × 12 cm) of nine trays, so that 90 animals (30 per tray) were placed in each of the three conditions. The three trays containing about 7 cm of clean sand were now covered (layered) with about 3 cm of the highly contaminated (estimated 8000 μg/g) substrate. The field installation was, therefore, complete and no further examination was made until 3 mo later.

Chemical Analyses

Exposure sediment samples were taken in several ways and analyzed by both infrared spectrophotometry (IR) and glass capillary gas chromatography (GC). Six samples of each treatment taken directly from the cement mixer were transferred to glass bottles and extracted overnight on a shaker with CCl_4. The CCl_4 extract was dried (Na_2SO_4) and analyzed for total hydrocarbons by IR (API 1958). Similar IR determinations were made on three sediment core (3.2 cm diam × 10 cm deep) samples at the time of installation, 3 mo later and at termination of the experiment (1 yr). Core samples for IR analyses (3 per condition × 3 time intervals) were mixed before extraction to provide information on the total amount of oil in the entire core. Gas chromatographic analyses were conducted on upper (0−5 cm) and lower (5−10 cm) sections of two additional sediment core extracts taken at installation and termination of the experiment.

Saturated and aromatic hydrocarbon samples of sediment were soxhlet extracted with benzene-methanol according to Clark and Finley (1973). Components in concentrated extracts (1 mL) were separated into saturated (40 mL of hexane) and aromatic (86 mL of 20% CH_2Cl_2 in hexane) hydrocarbon fractions using 15 g of activated silica gel (Grace Davison Chemical Co., 100−200 mesh, 150° overnight). Compounds in hydrocarbon fractions were concentrated under a stream of nitrogen and quantified on a Hewlett Packard 5840-A gas chromatograph containing a 30 m SP-2100 glass capillary column (J & W Scientific) and flame ionization detector. Individual hydrocarbons were corrected for losses based on the recovery of hydrocarbon analytical standards from control sediment. Prior to gas chromatographic analysis, samples of the saturated and aromatic hydrocarbon fractions were amended with 2,6,10-trimethyldodecane and hexamethylbenzene, respectively, to serve as internal standards. Samples were analyzed by temperature programing the gas chromatograph from 65 to 250°C at 4°/min following an initial hold at 65°C for 4 min.

Concentrated samples of the aromatic fraction also contained dibenzothiophenes. Diphenylsulfide (internal standard) was added to the samples and they were reanalyzed on a Hewlett Packard 5840-A gas chromatograph containing a sulfur specific flame photometric detector (FPD). Since all the compounds of interest contained only one sulfur atom per molecule, response in the FPD detector is proportional to the amount of sulfur present. Thus, dibenzothiophene and its corresponding mono-, di-, and trialkylated isomers were quantified using a calibration curve prepared from a standard of dibenzothiophene. In addition, the effect of the presence of hydrocarbons in the oil on the relative response of dibenzothiophenes in the FPD detector was assumed to be negligible (Maruyrma and Kakemoto 1978). Dibenzothiophene and its corresponding mono-, di- and trialkylated isomers were detected in Prudhoe Bay crude oil by gas chromatography/mass spectrometry (GC/MS).

Two samples of pooled clam tissue from each condition were digested in aqueous NaOH (4 mol/L) according to Warner (1976). The tissue digest was extracted with ethyl ether and after the solvent was evaporated it was fractionated by silica gel chromatography as described above for sediment analysis.

Quantification of all samples was on a μg/g (ppm) wet weight basis, where tissues contained about 80% water and sediment contained 16% water.

TABLE 1. Mean concentrations (μg/g, by IR) of petroleum hydrocarbons (± SD) in core samples of sediments taken at four time intervals.

		Core samples[a]		
	After mixing	At installation	3 mo later	1 yr later
Control	11.0 ±5.1 (6)[b]	11.0 ±5.1 (6)	16.6 ±4.4 (3)	60.1 ±7.4 (3)
Mixed-in	1,251.6 ±95.5 (6)	876.1 ±34.7 (3)	855.1 ±28.3 (3)	374.7 ±5.6 (3)
Layered-on	5,176.5 ±345.2 (6)	1,450.4 ±441.7 (3)	147.9 ±20.1 (3)	82.2 ±12.5 (3)

[a]Cores were mixed before extraction, thus integrating the concentrations at all depths. The high concentration material shown in the first column (after mixing) was only used in the top 3 cm of trays (about 10 cm deep) in the layered conditions, so core samples of this condition include sediment which was initially clean.

[b]Number of samples.

Analysis of Growth

Each clam, of the 270 installed, was measured in length (mm) and marked. The vernier caliper used to measure the length of individual clams was accurate to the nearest millimetre, but estimates to the nearest 0.2 mm could be made. At termination of the experiment, the meat of each group of clams was removed for hydrocarbon analyses and the shells were measured for increase in length. The growth of animals in the three conditions was subjected to covariance analysis with size difference (growth) as the dependent variable and preexposure size (score) as the covariate (Armitage 1977; Ostle 1974).

Results

Hydrocarbon Composition of Sediments

Control samples at the time of collection and 3 mo later exhibited very low levels of extractable organics, while 1 yr

TABLE 2. Mean concentrations (μg/g, by GC) of selected saturated and aromatic hydrocarbons (± SE) in sediment samples (n = 2) as a function of time and depth.

Condition	Length of exposure	Depth (cm)	Saturates	Aromatics
Control	1 yr	0–5	0.1±0.1	<0.1
		5–10	0.1±0.0	<0.1
Layered-on	Initial	0–5	36.6±11.9	21.9±7.6
		5–10	9.5±1.9	3.2±0.4
	1 yr	0–5	0.4±0.3	<0.2
		5–10	<0.1	<0.2
Mixed-in	Initial	0–5	57.9±4.7	22.1±1.1
		5–10	46.8±9.0	20.7±7.1
	1 yr	0–5	0.8±0.9	<0.6
		5–10	3.9±4.2	4.3±5.0

TABLE 3. Concentrations of selected hydrocarbons in Prudhoe Bay oil and mean[a] concentrations in two sediment samples completely mixed with oil, before and after 1 yr in the field.

			Sediments					
	Oil		Initial (μg/g)		Final 0–5 cm		Final 5–10 cm	
Compounds	mg/g	(%)	0–5	5–10	μg/g	(% Lost)	μg/g	(% Lost)
Saturates[b]								
(C_{11}–C_{26})	51.8	(48)	57.9	46.8	0.8	(99)	3.9	(92)
Aromatics								
Alkylbenzenes	32.0	(29)	4.5	4.8	<0.1	(100)	<0.1	(100)
Naphthalene	1.6	(2)	1.1	1.1	<0.01	(100)	<0.1	(100)
C_1-Naphthalenes[c]	5.5	(5)	7.0	6.6	<0.1	(100)	0.4	(94)
C_2-Naphthalenes	8.0	(8)	6.5	6.0	<0.2	(100)	1.7	(72)
C_3-Naphthalene	4.8	(4)	0.5	0.4	<0.03	(100)	0.2	(50)
Phenanthrene	0.6	(1)	0.8	0.6	<0.05	(100)	0.2	(67)
C_1-Phenanthrenes	1.7	(2)	1.7	1.2	<0.14	(100)	0.6	(50)
C_2-Phenanthrenes	1.7	(2)						
Total N + P[d]	23.8	(24)						
Dibenzothiophene	0.1				<0.0002	(100)	0.006	
C_1-DBT	0.3				<0.0006	(100)	0.025	
C_2-DBT	0.4				<0.0018	(100)	0.086	
C_3-DBT	0.5				<0.0024	(100)	0.140	
Total DBT	1.3	(1)	0.8[e]	0.8[e]			0.3	(63)[e]
Total measured hydrocarbons	109		80	68	0.8		7.3	

[a]Variability in initial samples was about 10% of the mean, but was as high as 100% in 1-yr samples.
[b]*n*-alkanes plus pristane and phytane.
[c]C_1-, C_2-, and C_3- represent mono-, di-, and trimethyl isomers of naphthalenes, phenanthrenes, and dibenzothiophenes (DBT).
[d]Total of the naphthalenes and the phenanthrenes.
[e]Estimated from percentage in the oil.

samples were about 4–5 times higher (Table 1). The drainage of oil from the trays and placement underwater on the beach produced a 30% loss between the time of mixing and the introduction of clams (Table 1). Little change occurred over the next three months, but after one year there was a loss of about 56%. The mixture of sediment and oil calculated to produce a concentration of 8000 μg/g (ppm) only produced 5176 μg/g when it was removed from the mixer. When this material was layered over clean sediment (7 cm) the entire core sample (10 cm) produced an initial concentration of 1450 μg/g. Cores taken 3 and 12 mo later were reduced to 10 and 6%, respectively, of the installation value.

Additional core samples were first sectioned into top 5 cm and bottom 5 cm, and then extracted and analyzed by glass capillary gas chromatography for saturate and aromatic hydrocarbons (Table 2). From the layered condition both saturates and aromatics could be found at low concentrations (3–9 μg/g) in the bottom section, which did not receive oil directly. After 1 yr, very small amounts of *n*-alkanes from C_{14} to C_{24}, as well as pristane and phytane, were found in the top

TABLE 4. Concentrations of aromatic petroleum hydrocarbons in *Protothaca staminea* exposed in the field for 1 yr to oil mixed with sediment.

Compound	Tissue concentrations (ng/g)		
Isopropylbenzene	<1.1		[a]<2.5
1-ethyl-4-methylbenzene	<1.1		<2.5
1,2,4-trimethylbenzene	<1.1		<2.6
sec-butylbenzene	<1.1		<2.6
1-methyl-4-isopropylbenzene	<1.4		<3.3
Indan	<1.3		<3.1
1,3-dimethyl-5-ethylbenzene	<1.1		<2.6
1,2-dimethyl-4-ethylbenzene	<1.1		<2.6
1,2,4,5-tetramethylbenzene	<1.0		<2.4
1,2,3,5-tetramethylbenzene	<1.1		<2.6
Naphthalene	7.4		<2.6
2-methylnaphthalene	20.7		<2.4
1-methylnaphthalene	40.3		<2.7
1-ethyl+2-ethylnaphthalene	40.0		12.0
2,6-dimethylnaphthalene	32.3		52.7
1,3-dimethylnaphthalene	76.2		126.5
1,7-dimethylnaphthalene	38.4		71.8
1,4-dimethylnaphthalene	5.1		7.6
1,2-dimethylnaphthalene	63.4		104.5
2,3,6-trimethylnaphthalene	44.3		72.9
Phenanthrene	81.6		52.9
2-methylphenanthrene	58.1		98.5
Totals	507.8		599.9
Mean ± SD		553.8 ±65.2	
Dibenzothiophene (DBT)	2		
C_1-DBT (3)[b]	7		
C_2-DBT (9)	16		
C_3-DBT (12)	21		
Total dibenzothiophenes	46		

[a]Limit of detection.
[b]Number of isomers quantitated.

layer only. Sediment mixed with oil retained very small amounts in the surface layer after 1 yr (1–3%), but higher concentrations in the bottom 5 cm (8–16%).

Table 3 shows the concentrations of some hydrocarbon components in the crude oil, grouped as classes of compounds and their percent contribution to the total measured components. The measured compounds fell into four groups as follows: (1) 48% saturates, (2) 29% alkylbenzenes, (3) 19% naphthalenes, and (4) 5% phenanthrenes. The sulfur containing compounds, dibenzothiophene and alkyl-derivatives of it, compose only about 1% of the total measured components in the oil. The compounds listed in Table 3 represent only about 10% of all components in crude oils. Calculations for percent contribution of the compounds shown are based on only those hydrocarbons measured (109 mg/g of oil). It is then possible to compare the percent distribution of hydrocarbons in the initial and final sediment samples back to their distribution in the original crude oil.

Since very little contamination remained in the final sediment samples of the layered oil condition (Table 2), only the mixed oil system is compared in Table 3. Initially, the majority of contamination in the top and bottom layers of this sediment was from saturated compounds, although significant levels of alkylbenzenes, naphthalenes and phenanthrenes were also present. Dibenzothiophenes were estimated, based on their percentage in the oil (1%), to be present at about 0.8 μg/g. After one year in the intertidal zone of Sequim Bay, Washington, total hydrocarbon concentrations in the top layer had decreased to about 1% of initial values, but the bottom layer contained about 10% of the original concentration.

Saturated hydrocarbons constituted about 50% of the retained components. The alterations in saturates, where there was a 92% loss, may be partially the result of microbial degradation (Blumer and Sass 1972; Anderson et al. 1978). Ratios of C_{17} to pristane in initial sediment cores were 1.34–1.54, but in the bottom section of final cores the ratio had decreased to 0.33. Similarly, the C_{18} to phytane ratio decreased from initial values of 2.06–2.10 to 0.29 after 1 yr in the bottom of the sediment tray. Measurable levels of aromatics were only found in the lower layer, and those remaining were of relatively high molecular weight. The rates of hydrocarbon release in this study compare closely with those described earlier (Anderson et al. 1978). There were no detectable levels of naphthalenes or phenanthrenes found in surface oiled sediments after 204–220 d in the intertidal zone, but finer sediments mixed with oil still contained over 40% of the hydrocarbons after 290 d in the field (Anderson et al. 1978). In the present study, naphthalene was completely lost and isomers of naphthalene were lost in inverse proportion to the number of alkyl-groups. While mono- and dimethylnaphthalenes were prominent in the initial sediments, their loss was greater than that of the trimethylnaphthalenes and higher molecular weight compounds. Phenanthrene, 2-methylphenanthrene, and dibenzothiophenes were still present at 50–67% of initial levels.

Hydrocarbon Content of Clam Tissue

There were no apparent differences between controls and the two treatment groups in the concentrations or distributions of saturated compounds in the tissues of clams. No detectable levels (<3 ng/g) of monoaromatic compounds were found in any of the samples of clam tissue. No detectable levels of petroleum hydrocarbons were found in the tissues of clams exposed to the layer of oiled sediment. Naphthalene and monomethylnaphthalenes were present in one of the two pooled tissue samples from animals in the mixed in oil group (Table 4). Ethylnaphthalenes and isomers of greater molecular weight were present in both samples. The majority of the contamination was due to the presence of several isomers of dimethylnaphthalene (over 50%). About 8% of the contamination in the one tissue sample analyzed was from the sulfur containing compounds, dibenzothiophenes. Samples of clams from the control and layered oil groups did not contain detectable (<0.4 ng/g) levels of dibenzothiophenes.

Growth of Clams

No significant growth was recorded when a small group (10 animals from each condition) of clams was sampled after 3 mo in the field. Mean growth of clams (± standard devi-

TABLE 5. Analysis of variance and covariance for *P. staminea* data on initial size (covariate) and growth.

Group	*n*	Mean growth (mm)	Mean adjusted for covariate
Control	31	10.76	10.69
Mixed	32	8.62	8.75
Layered	48	9.91	9.87

Covariance analysis

Source	df	ms	*f*	Tail area prob.
Covariate	1	197.90	53.46	0.0000
Treatments	2	30.01	8.11	0.0005
Error	107	3.70		

Contrast	With covariate	
	T[a]	$P(T)$[b]
Control vs. treatment	−3.37	0.0010
Mixed vs. layered	2.55	0.0121

[a] T represents the magnitude of the difference produced in the contrast.

[b] $P(T)$ is the probability that the interaction is from chance alone.

ations and number of clams from 80 possible) for the three groups after one year was as follows: (1) control, 10.8 ± 2.3 mm; $n = 31$, (2) mixed, 8.6 ± 2.4 mm; $n = 32$, and (3) layered, 9.9 ± 2.3 mm; $n = 48$. To test the appropriateness of covariance analysis on score (growth), with pre-score (initial size) as a covariate, the following steps were taken. First, regression analysis was performed to see if score differential varied with pre-test score in the three experimental groups. Growth decreased as size increased in each case, and the regression was significant ($P < 0.02$) in all three conditions. Since growth was dependent on pre-experiment size, covariance analysis seemed to be appropriate. Prior to the analysis, two assumptions upon which analysis of covariance is based were tested. Analysis revealed that the treatments were not affected by the covariate (i.e. the experimental units were randomly allocated among treatments) and there was no reason to suspect non-homogeneity of slopes between cells ($P = 0.90$). As may be seen in Table 5, both the covariate and the treatment are highly significant.

Another way to examine multiple treatment means is to analyze single degrees of freedom. In this case, there are three treatments and so there are 2 df. These can be partitioned orthogonally so that the tests are independent and inflated alpha levels are not a problem. In this case, the most logical way to partition would be to test control vs. treatments and mixed vs. layered. The first degree of freedom tests whether growth in the control group is different from growth in the treated groups. The second degree of freedom tests if growth in the mixed sediments is different from growth in the layered sediment. The results of these analyses (Table 5) show that clam growth in oil treated sediments was significantly (0.001 level) slower than in untreated sediments. In addition, growth in sediments where the oil was mixed into the sand was significantly (0.01 level) slower than growth in sediments where the oil was layered on the surface.

Discussion

SEDIMENT HYDROCARBONS

It is clear that initial exposure conditions in this experiment were relatively harsh, as total levels of extractable organics were initially 876 and 1450 μg/g for the mixed and layered systems, respectively. Analyses of total hydrocarbons (IR) showed that about 10% of the oil remained in the layered system after 1 yr, but as much as 56% was still present in the mixed system. This latter value may be high, since gas chromatographic analyses of replicate cores from the mixed oil treatment indicated nearly complete loss of measured hydrocarbons in the top section versus a 90% loss in the bottom section. Since the IR method is nonspecific for petroleum hydrocarbons, a portion of the indicated final concentration may be due to the input of detrital material accumulated over the one year period.

Saturated hydrocarbons, which are the dominant compounds in the original oil and the initial sediments, were preferentially lost. Since microbial degradation acts more rapidly on straight chain hydrocarbons (C_{17} and C_{18}) than on branched chain hydrocarbons (pristane and phytane), it was not surprising that the ratios for the former to the latter decreased from about 1.3−2.1 to about 0.3 after 1 yr. Very similar alterations in these ratios were noted by Anderson et al. (1978) during an earlier field experiment with oiled sediment in the same intertidal zone. The ratios of nC-17/pristane (3.3) and nC-18/phytane (2.4) in the reference mousse from the Amoco Cadiz spill were representative of fresh oil, but samples of intertidal sediment collected about 20 d after the spill in Aber Wrack showed ratios of 0.3 and 0.2, respectively (Calder and Boehm 1981). The extent of apparent biodegradation demonstrated in this short period is equivalent to that observed in the lower (5−10 cm) sections of our sediment samples after 1 yr.

No detectable amounts of any aromatics were present in the upper layer (0−5 cm) of the mixed system. While alkylbenzenes and naphthalene were lost completely from the lower layer, some of the mono-methylnaphthalenes (6%) still remained. Greater retention was observed with further substitution of the diaromatic ring, since 28% of the C_2-naphthalenes and 50% of the C_3-naphthalenes were still present. Continuing this trend, 67% of the triaromatic compound, phenanthrene was lost from the sediment, but only 50% of a monomethyl isomer was released during the field exposure.

Insufficient data are available to evaluate this pattern within the dibenzothiophenes, but the total loss of the parent compound and all alkyl-derivatives was estimated to be about 63%. Calder and Boehm (1981), studying Aber Wrac'h over a 1-yr period, reported that dibenzothiophenes were the most prominent aromatic compounds and they showed a loss of about 60% in 12 mo. Teal et al. (1978) noted that 7 mo after marsh sediments were impacted by fuel oil, the naphthalene content decreased by 93% and C_1-naphthalenes by about 90%, while more highly substituted naphthalenes and the alkylphenanthrenes all decreased by about 80%.

Grahl-Nielsen (1979) reported that with time the relative percentage contribution of three classes of aromatic

hydrocarbons tend to favor increases in phenanthrenes and dibenzothiophenes, as naphthalenes are lost, presumably by degradation. Grahl-Nielsen et al. (1978) sampled water during 6 mo after a spill and showed decreases in naphthalenes (60−20%), increases in dibenzothiophenes (20−30%), and stability in the phenanthrenes (10−20%). Dimethyl derivatives were the dominant forms in each of the three classes of compounds.

Tissue Hydrocarbons

Very little tissue contamination was observed when clams were removed from the oiled sediments after one year in the field (Table 4). No detectable amounts of petroleum components were present in clams living in the layered oil system. As with the oiled sediment, alkylbenzenes and naphthalene were absent from clam tissues. The lowest molecular weight aromatics found in both tissue samples were the ethylnaphthalenes. Most (51%) of the contamination was from nine isomers of dimethylnaphthalene, but significant levels of C_3-naphthalenes, phenanthrenes, and dibenzothiophenes were also present. Aside from the peak accumulation of C_2-naphthalenes, there seems to be a pattern of increased retention with increasing molecular weight, within a hydrocarbon class (naphthalenes, phenanthrenes, and dibenzothiophenes).

This pattern is subject to bias by the differential in the numbers of isomers quantified (1−12). It is necessary to compare the content in tissues to the initial concentrations of the various groups of isomers in the oiled sediments to determine whether or not this bias is real. The initial sediments contained about the same amounts of C_1- and C_2-naphthalenes, but 1/10 as much C_3-naphthalenes. Monomethylnaphthalenes were completely lost from sediment and C_3-naphthalenes were retained to the greatest extent (50%). Therefore, the high retention of C_2-naphthalenes in tissues represents a preferential retention of compounds of intermediate solubility within the naphthalenes. Monomethylphenanthrene was present at higher concentrations than the parent compound in the oil, the initial and final sediments and in one of two tissue samples. Therefore, either increased availability or increased retention could be responsible for the one case of higher tissue content of 2-methylphenanthrene than the parent compound. The very low levels of dibenzothiophenes in oil, sediment and tissue do not allow accurate evaluation of relative retention with increased alkylation of the parent compound.

There have been reports that dibenzothiophenes may be preferentially retained in tissues, compared to other aromatic classes of hydrocarbons (Lake and Hershner 1977; Warner 1975; Grahl-Nielsen et al. 1978). The ratios of tissue concentrations to final sediment concentrations for the three hydrocarbon classes (phenanthrenes, alkylnaphthalenes, dibenzothiophenes) can be compared. These ratios were 0.18 for phenanthrenes, 0.16 for alkylnaphthalenes, and 0.15 for dibenzothiophenes. The sulfur-containing dibenzothiophenes were apparently not retained to any greater extent than other high molecular weight aromatic hydrocarbons.

Effects on Growth

About 40−60% of the clams were lost by either predation or lateral movement. Since the maximum recovery was from an oil-treated system and the minimum was from the control trays, treatment condition did not seem to be responsible. All statistical treatments of the growth data indicated that oil treatments served to suppress the growth rate of small *Protothaca staminea*. When oil was mixed into sediment (10 cm), the impact on growth rate was greater than a surface (3 cm) oiling, even though the oil level in the surface layer was significantly higher. Apparently, the rapid loss of petroleum components from the surface of sediments decreased the impact on growth, which occurred over a 1-yr period. No doubt a balance exists between the extent of surface oiling that can initially be tolerated by the animals and the rate of hydrocarbon loss from this layer. Earlier studies (Roesijadi et al. 1978) have shown that larger specimens of this clam were not significantly affected by oiled sediment (887 μg/g) and did not accumulate as much contamination (0.18 μg/g) in 60 d as was exhibited in the present 1-yr experiment. In a very recent study (Augenfeld et al. 1981), we reported that larger *P. staminea* exhibited greater tolerance to oiled sediment than *Macoma inquinata* during a 54-d field exposure. In this study and an early report (Roesijadi and Anderson 1979), it was shown that *Macoma* is more likely to suffer mortality, decreased condition index, and altered free amino acid levels than *Protothaca* when exposed to oiled sediments in the field. Other researchers have shown that *Macoma balthica* is relatively sensitive to oil in seawater or sediments (Stekoll et al. 1980). It appears that detritivorous clams (e.g. *Macoma*) are in general more sensitive than filter-feeders like adult *P. staminea*. However, we have shown that growth in small *P. staminea* can be a sensitive indicator of the impact on a population from oiled sediment, and that the degree of contamination from high molecular weight aromatic hydrocarbons may be correlated with the extent of stress.

Acknowledgments

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through interagency agreement EPA-82-D-X0533 to the Pacific Northwest Laboratory, it has not been subjected to agency review and therefore does not necessarily reflect the views of the agency and no official endorsement should be inferred.

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Hepatic Microsomal Monooxygenase Activity and the Biotransformation of Hydrocarbons in Deep Benthic Fish from the Western North Atlantic[1]

JOHN J. STEGEMAN

Biology Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

STEGEMAN, J. J. 1983. Hepatic microsomal monooxygenase activity and the biotransformation of hydrocarbons in deep benthic fish from the western North Atlantic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 78–85.

Microsomal electron transfer components cytochrome P-450, cytochrome b_5, NADPH-cytochrome c (P-450) reductase activity and NADH-cytochrome c (b_5) reductase activity were present in hepatic microsomes from several species of deep-sea fishes sampled between 1400 and 3200 m deep in the North Atlantic. The specific content of cytochrome P-450 varied among the species but was within the range observed for shallow-water fishes. The specific content was the highest in the deepest sampled species, *Coryphaenoides armatus* (0.25 nmol/mg microsomal protein). Hepatic microsomes from this species also exhibited little or no putative cytochrome P-420 whose presence suggested some degradation of cytochrome P-450 in the other species. Ethoxyresorufin *O*-deethylase and benzo[*a*]pyrene hydroxylase activities were high in several species, particularly *Coryphaenoides armatus*. Strong inhibition of benzo[*a*]pyrene hydroxylase activity by α-naphthoflavone was demonstrated in some species. The data suggest that some hepatic cytochrome P-450 in *Coryphaenoides armatus* (and possibly *Coryphaenoides leptolepis* and *Bathysaurus mollis*) but not in *Coryphaenoides rupestris* or *Antimora rostrata* may have been induced by environmental chemicals in the deep sea. As in other teleost fishes, *Coryphaenoides* hepatic microsomes metabolized benzo[*a*]pyrene in vitro with a high specificity for the benzo-ring, suggesting the capacity to form mutagenic derivatives of some hydrocarbons efficiently.

STEGEMAN, J. J. 1983. Hepatic microsomal monooxygenase activity and the biotransformation of hydrocarbons in deep benthic fish from the western North Atlantic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 78–85.

Les composants de transfert d'électrons microsomiques cytochrome P-450, cytochrome b_5, l'activité de la NADPH-cytochrome c (P-450) réductase et de la NADH-cytochrome c (b_5) réductase sont présents dans les microsomes hépatiques de plusieurs espèces de poissons des profondeurs capturées entre 1400 et 3200 m dans l'Atlantique nord. Un contenu spécifique en cytochrome P-450 varie d'une espèce à l'autre, mais se situe dans la gamme observée chez des poissons d'eaux peu profondes. Le contenu spécifique est maximal chez l'espèce capturée à la plus grande profondeur, *Coryphaenoides armatus* (0,25 nmol/mg de protéines microsomiques). En outre, les microsomes hépatiques de cette espèce ne montrent que peu ou pas de cytochrome P-420 putatif dont la présence laisse supposer une certaine dégradation du cytochrome P-450 chez les autres espèces. L'activité de l'éthoxyrésorufine *O*-dééthylase et de la benzo[*a*]pyrène hydroxylase est prononcée chez plusieurs espèces, en particulier *Coryphaenoides armatus*. Chez certaines espèces, on a observé une forte inhibition de l'activité de la benzo[*a*]pyrène hydroxylase par α-naphthoflavone. Les données donnent à penser qu'une certaine quantité de cytochrome P-450 hépatique chez *Coryphaenoides armatus* (et possiblement chez *Coryphaenoides leptolepis* et *Bathysaurus mollis*) mais non chez *Coryphaenoides rupestris* ou *Antimora rostrata* ait pu être causée par des substances chimiques ambiantes en eaux profondes. Comme chez les autres téléostéens, les microsomes hépatiques de *Coryphaenoides* métabolisent le benzo[*a*]pyrène in vitro, avec haute spécificité pour le noyau benzo, ce qui suggère une capacité à former efficacement des dérivés mutagènes de certains hydrocarbures.

Received March 18, 1982
Accepted September 28, 1982

Reçu le 18 mars 1982
Accepté le 28 septembre 1982

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6850)
Imprimé au Canada (J6850)

POLYNUCLEAR aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), pesticides, and other organic compounds with anthropogenic origins are widely present as contaminants in marine waters and sediments. Such compounds occur at appreciable levels in coastal, particularly urban, environments, but they are also present at lower concentrations in sediments on the continental slope or in the deep sea (LaFlamme and Hites 1978). the residence, transformation, and effects of these compounds in the deep sea depend upon a variety of biogeochemical processes, knowledge of which should ultimately indicate the assimilative capacity and sensitivity of this remote environment to organic contaminants. In contrast with surface and coastal waters, photocatalytic alterations are ruled out in the deep sea. Microbial activity is also strongly affected in much of the deep sea by the limited supply of organic carbon, as well as by low temperature and increased hydrostatic pressure (Jannasch and Wirsen 1982). Low concentrations of organic carbon sources in the deep sea could well limit the transformation of xenobiotics such as PAH by microbes, although this prospect has not been confirmed. The biotransformation of xenobiotics by animals could be a significant factor in the overall fate of these compounds in the deep sea, as well as with their effects on the biota in these regions.

A critial point of interaction between organic foreign compounds such as PAH and the biota is the cytochrome P-450-dependent monooxygenase system. Cytochrome P-450 exists in multiple forms that have diverse catalytic and physiological functions. Included among the variety of reactions catalyzed by cytochrome P-450s are the monooxygenase reactions that initiate the biotransformation of PAH and other hydrocarbons. The functional groups resulting from addition of $1/2\ O_2$ may aid in the detoxication and elimination of PAH, but such oxidation can also result in formation of chemical species that are more reactive and toxic (e.g. mutagenic) than the parent compound. Various foreign compounds, including selected PCBs and PAH, can induce the formation of additional cytochrome P-450 with a high specificity for PAH, thereby augmenting the capacity for the metabolism of these compounds (Bend and James 1978; Stegeman 1981a). Due to their role in mediating foreign compound metabolism and effects, their potential for indicating the presence of biochemically significant levels of various organic pollutants, and the prospect for continued disposal of wastes at sea, it is important to assess the characteristics of cytochromes P-450 and the capacity for biotransformation of PAH in animals in the deep sea. This communication provides the first description of microsomal electron transfer systems and cytochrome P-450 in liver of deep sea fishes, and describes the pattern of metabolism of the model PAH benzo[*a*]pyrene carried out by one species, the rattail *Coryphaenoides armatus*.

Materials and Methods

CHEMICALS

7,8-Benzoflavone (α-naphthoflavone; ANF) was obtained from Aldrich Chemical Company, Milwaukee, WI. [^{3}H]-Benzo[*a*]pyrene (BP) was obtained from Amersham-Searle, Skokie, IL, and was purified as in Binder and Stegeman (1981). Resorufin was obtained from MCB Chemical Company and was acetylated with acetic anhydride, purified by chromatography on silica gel, deblocked by hydrolysis with NaOH and recrystallized from dimethylformamide as described in detail elsewhere (Stegeman et al. 1982). 7-Ethoxyresorufin (ER) was synthesized according to the methods of Prough et al. (1978). Both compounds were judged pure by thin-layer chromatography and nuclear magnetic resonance spectroscopy. Reduced nicotinamide adenine dinucleotide phosphate (NADPH) was obtained from the Sigma Chemical Co., St.Louis, MO.Materials for high pressure liquid chromatography (HPLC) were obtained as in Tjessem and Stegeman (1979).

ANIMALS

Deep benthic species were obtained by trawling with a 12.5 m Gulf of Mexico shrimp trawl on Cruise 93 of the R/V *Oceanus*, March 28–31, 1981, in the vicinity of 39°N and 70°W (Table 1). All members of a given species were taken in a single trawl, except for *Coryphaenoides leptolepis*, which came from two trawls. Animals were retrieved through cold waters (surface temperatures near 6°C) and were dissected within minutes after reaching the deck. The animals

TABLE 1. Deep benthic fish species. The three species of *Coryphaenoides* are closely related forms, commonly called rattails, that at times have been classed in separate genera, i.e. *Chalinura leptolepis* and *Nematonurus armatus*. The generic name *Coryphaenoides* is applied to all three species as originally done, and as most recently suggested by Iwamoto and Stein (1974).

Species	(N)	Trawl	Sampling[a] location		Average depth (m)
			North	West	
Coryphaenoides rupestris	(1)	903	39°48′	69°45′	1410
Antimora rostrata	(5)	903	"	"	1410
Coryphaenoides leptolepis	(1)	909	38°58′	69°50′	2900
Coryphaenoides leptolepis	(2)	902	38°45′	70°03′	3050
Bathysaurus mollis	(1)	901	38°43′	69°58′	3100
Coryphaenoides armatus	(4)	900	38°35′	69°58′	3245

[a]Position of the ship at the start of the trawl.

were adult fish with some minimal signs of life (beating heart). Gonads of the animals were not obviously developed. Livers were removed from the animals within 15 min of arriving on deck. Portions were immediately frozen in liquid N_2, then stored at −80°C until microsomes were prepared ashore, within 8 d.

Tissue Preparation

All procedures were carried out at ice temperature. Livers of deep-sea species were thawed, tissues were finely minced and homogenized in 5 vol of 50 mmol potassium phosphate/L, pH 7.4, containing 1.15% KCl. Subcellular fractionation was accomplished as previously described (Stegeman and Binder 1979), except that samples were centrifuged twice at 2 500 and twice at 10 000 × *g* to aid in separating and removing the abundant lipid pellicle. Microsomal fractions were resuspended in 50 mmol Tris/L containing 1 mmol EDTA/L, 1 mmol dithiothreitol/L and 20% glycerol by volume. Preparations were used directly or were stored in liquid N_2 until use.

Enzyme Assays

Benzo[*a*]pyrene hydroxylase activity was assessed by determining the total production of water soluble derivatives of [^{3}H]BP, accomplished by a microscale radiometric procedure described previously (Binder and Stegeman 1980). Assay temperature for deep sea samples was 20°C and pH was 7.4. Temperature and pH optima for one of these species (*C. armatus*) were determined previously using freshly prepared samples assayed at sea (unpublished observations). The influence of ANF on BP metabolism was determined by adding ANF in 2 µL methanol to the BP hydroxylase reaction mixture just prior to addition of [^{3}H]BP. Blanks consisted of reaction mixtures minus cofactor or complete reaction mixtures with boiled enzyme. Assays were carried out in triplicate under red light.

Ethoxyresorufin (ER) *O*-deethylase activity was measured using a 1.0 mL reaction mixture containing 2 µmol ER/L, 0.1 mol Tris/L, pH 8.0, 0.1 mol NaCl/L, and 3−8 mg of microsomal protein/mL. Substrate concentration, pH and ionic strength used were determined to be optimal for a shallow water fish species. The reaction at 25°C was initiated with NADPH at a final concentration of 0.5 mmol/L and the appearance of resorufin was monitored at 572 nm using a Cary 118C recording spectrophotometer. The extinction coefficient of resorufin was experimentally determined to be 73 $mmol \cdot L^{-1} \cdot cm^{-1}$.

NADPH-cytochrome c reductase activity was assayed at 25°C by a modification of the method of Phillips and Langdon (1962) with a reaction mixture containing 0.175 mmol NADPH/L, 80 µmol horse heart cytochrome c/L and 1 mmol KCN/L in 0.2 mol potassium phosphate buffer/L, pH 7.7. NADH-cytochrome c reductase activity was assayed using the conditions for NADPH-cytochrome c reductase, with 0.25 mmol NADH/L replacing 0.275 mmol NADPH/L. Succinate-cytochrome c reductase activity was assayed according to Green et al. (1955). Reaction mixtures of 0.50 mL volume contained 10 mg bovine serum albumin/mL, 80 µmol cytochrome c/L, and 1 mmol KCN/L in 0.02 mol phosphate buffer/L, pH 7.4. Reactions at 25°C were initiated by addition of sodium succinate to a final concentration of 5 mmol/L. Reduction of cytochrome c

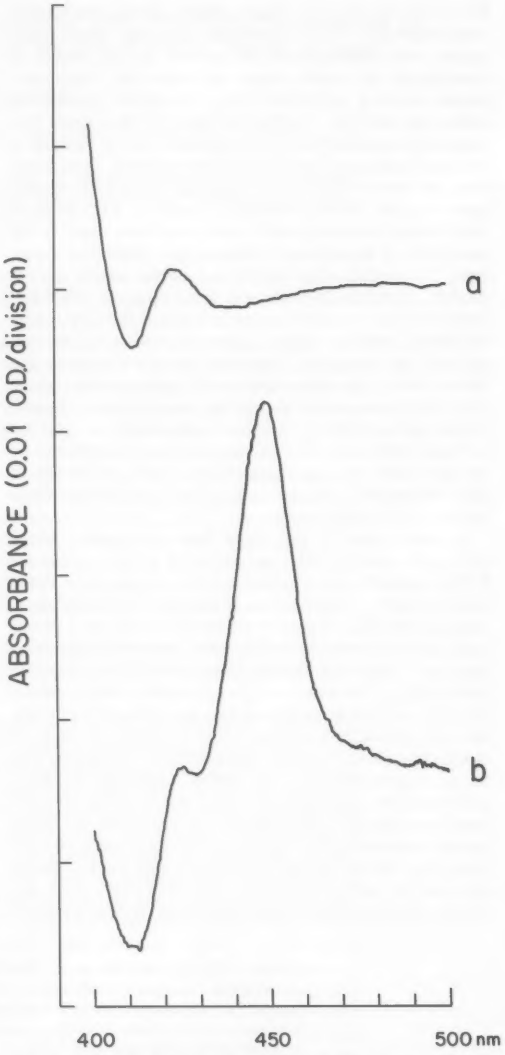

FIG. 1. Optical spectra of cytochrome b_5 (a) and cytochrome P-450 (b) in hepatic microsomes of *Coryphaenoides armatus*. Both spectra were obtained with microsomes from the same individual. The concentration of protein in the cuvettes was 1.03 mg/mL. In obtaining the P-450 spectrum both NADH (0.34 mg/mL) and CO were balanced in sample and reference cuvettes and the sample was reduced with $Na_2S_2O_4$.

TABLE 2. Hepatic microsomal electron transfer components in deep-sea fish.

Species (N)		Microsomal yield (mg/g tissue)[a]	Cytochrome P-450 (nmol/mg)[b]	Cytochrome b_5 (nmol/mg)[b]	NADPH-cytochrome c reductase (units/mg)[c]	NADH-cytochrome c reductase (units/mg)[c]
C. armatus	(4)	10.6±4.5[d]	0.25±0.06	0.04±0.03	39.8±6.4	32.5±15.2
C. leptolepis	(3)	8.5±5.7	0.15±0.06	0.03±0.02	17.7±2.9	26.3±18.1
A. rostrata	(5)	2.6±1.1	0.08±0.02	0.02±0.01	9.4±3.8	97.0±42.8
B. mollis	(1)[e]	1.8	0.09	0.02	9	139
C. rupestris	(1)[e]	2.5	0.08	0.01	5	100

[a]Milligrams microsomal protein per gram liver.
[b]Nanomoles cytochrome P-450 or b_5 per milligram microsomal protein.
[c]Units are nanomoles cytochrome c reduced per minute per milligram microsomal protein ($nmol \cdot min^{-1} \cdot mg^{-1}$).
[d]Values represent means ± SD.
[e]Data for single specimens of these individuals are presented because of the difficulty in obtaining such samples and consequently their unique nature.

at 550 nm was followed using a Cary 118C recording spectrophotometer.

Cytochrome b_5 was estimated from NADH difference spectra obtained as before (Stegeman et al. 1979). Cytochrome P-450 was estimated by $Na_2S_2O_4$-difference spectra of CO-treated samples that had also been balanced with respect to NADH, thus eliminating contribution of both cytochrome b_5 and hemoglobin to absorbance near 420 nm. Resuspensions for analysis of both cytochrome b_5 and P-450 contained 0.3 to about 1 mg microsomal protein/mL.

Practical limits of detection for the assays as used, dependent on the amount of microsomal protein, were: cytochrome P-450, 0.01 nmol/mg microsomal protein; cytochrome b_5, 0.005 nmol/mg; reductases, 0.23−0.37 nmol cytochrome c reduced $\cdot min^{-1} \cdot mg^{-1}$; ER *O*-deethylase, 0.01−0.03 nmol resorufin $\cdot min^{-1} \cdot mg^{-1}$; BP hydroxylase, 0.3−1.2 pmol $\cdot min^{-1} \cdot mg^{-1}$. Protein was determined according to the method of Lowry et al. (1951).

HIGH PRESSURE LIQUID CHROMATOGRAPHY

Metabolites of [^{3}H]BP were obtained by incubation in vitro with hepatic microsomes. Reaction mixtures of 0.4 mL final volume containing 60 μmol BP/L with a specific activity of about 3.22 GBq/mmol (87 mC/mmol), 0.375 mg NADPH/mL and about 0.4 mg microsomal protein/mL were incubated for 20 minutes and the metabolites were extracted and prepared as before (Tjessem and Stegeman 1979) with final dissolution in 40−100 μL acetonitrile. Zero-time blanks were treated in the same fashion. Separation of metabolites was achieved on a DuPont Zorbax ODS column using a DuPont LC 850 chromatograph. Elution of metabolites was accomplished by running a gradient from 40 to 85% of acetonitrile in water. Metabolites were identified based on coelution with authentic standards and [^{3}H] in eluted fractions was quantified by liquid scintillation spectroscopy. All procedures were carried out under red light. The mean recovery of separate tritiated metabolites carried individually through the entire procedure was about 70% and the data have been corrected for this.

Results

Optical difference spectroscopy under appropriate conditions revealed the presence of cytochromes P-450 and b_5 in hepatic microsomes from each of the deep-sea species examined. The spectra obtained for CO-bound, reduced microsomes from one species (*Coryphaenoides armatus*) were quite typical for vertebrate hepatic microsomes, and they had little or no absorbance near 420 nm (Fig. 1). However, samples from some other individuals of this species and the samples from other species showed varied amounts of absorbance at wavelengths between 420−424 nm. It is unlikely that the latter absorbance was due to cytochrome b_5 as any contribution from this chromophore should have been balanced by the addition of NADH to both sample and reference cuvettes. Rather, it is quite probable that the absorbance was due to degraded cytochrome P-450, or cytochrome P-420. Whatever the source of absorbance near 424 nm, the wavelength of the absorption maximum and the amount of absorbance near 450 nm could be determined without ambiguity.

In all cases the absorption maximum of cytochrome P-450 was between 449 and 450 nm. The specific contents of cytochromes P-450 and b_5 and the levels of NADPH- and NADH-dependent cytochrome c reductase activity in hepatic microsomes of the deep sea fish are presented in Table 2. Microsomal yield and the levels of these microsomal electron transfer components in the two rattails *C. armatus* and *C. leptolepis* were within the range of values obtained for numerous coastal marine and freshwater fish (see Stegeman 1981a). In the other three species in Table 2, the yield of microsomal protein and the levels of these components were substantially lower, with exception of NADH-cytochrome c reductase activity which was at least 3-fold higher in these species than in *C. armatus* and *C. leptolepis*.

Some of the "excess" NADH-dependent reductase activity in the *Antimora*, *Bathysaurus*, and *Coryphaenoides* species could be associated with greater contamination of these latter microsomal preparations by mitochondrial fragments. The levels of succinate-cytochrome c reductase activity, a mitochondrial marker, in microsomal preparations from these species ranged between 2 and 3.5 $nmol \cdot min^{-1} \cdot mg^{-1}$, whereas the activity was about 0.5 and 1.0 $nmol \cdot min^{-1} \cdot mg^{-1}$ in

TABLE 3. Hepatic microsomal monooxygenase activity in deep-sea fish.

Sample microsomes (N)		ER O-deethylase[a]		BP-hydroxylase[a]		Percent of total BPH activity with 10^{-4} mol ANF/L
		units/mg	units/nmol P-450	units/mg	units/nmol P-450	
S. gairdneri[b]						
control	(5)	0.10±0.07[b]	0.32±0.09	0.011±0.005	0.04±0.01	—
3-MC	(7)	3.63±0.09	6.48±0.92	0.213±0.005	0.38±0.05	—
C. armatus	(4)	0.285±0.123	1.18±0.62	0.109±0.067	0.47±0.34	3±2
C. leptolepis	(3)	0.079±0.029	0.51±0.01	0.019±0.004	0.13±0.02	10±6
A. rostrata	(5)	0.056±0.019	0.72±0.31	0.003±0.002	0.04±0.02	153±159
B. mollis	(1)	ND[d]	ND	0.031	0.34	11
C. rupestris	(1)	0.012	0.15	0.002	0.02	102

[a]Units of activity are either nanomoles resorufin produced per minute or nanomoles ^{3}H−BP metabolites produced per minute.
[b]Data for rainbow trout (*Salmo gairdneri*) are from Stegeman et al. (1981).
[c]Values are means ± SD of results with N individuals.
[d]ND = Not detectable; i.e. < 0.023 units/mg.

microsomes from *C. armatus* and *C. leptolepis*, respectively. However, the levels of succinate-cytochrome c reductase activity were in all cases low enough to allow the conclusion that only a small amount of NADH-dependent activity might be due to mitochondrial contamination. That low microsomal yield resulted from failure to sediment microsomal vesicles was suggested by analysis of NADPH-cytochrome c reductase activity in cytosolic fractions. Whereas a large percentage of the total activity was present in microsomes of *C. armatus* and *C. leptolepis*, microsomal preparations of the other species contained only 10−20% of the total activity, the remainder being present in the supernatant fractions. Although such effects might be attributed to differences in particle density and hence sedimentation, it is of course also possible that the differences in data in Table 2 to some degree reflect inherent differences between the species.

As with the specific content of cytochrome P-450, monooxygenase specific activities were highest in *C. armatus* (Table 3). Levels of ER *O*-deethylase and BP hydroxylase activity per mg microsomal protein were higher in this species than the levels commonly seen in many untreated shallow water or freshwater fish. For example, these activities in control rainbow trout (*Salmo gairdneri*) liver (Table 3), were 3 to 10 times lower than in *C. armatus*. Monooxygenase specific activities in the other species were all equal to or lower than in control trout. As noted above, a possible degradation may have resulted in lower specific content of cytochrome P-450, hence lower monooxygenase activity per mg protein. Yet barring a selective degradation of different forms of cytochrome P-450, the samples can be used to estimate the catalytic efficiency of cytochrome P-450 in these animals. The activities per nmol of cytochrome P-450 for both ER *O*-deethylase and BP-hydroxylase were still 3 and 10 times higher in *C. armatus* than these activities in control trout. Significantly, the BP-hydroxylase activity per nmol of cytochrome P-450 was even higher than that in 3-methylcholanthrene-induced trout. BP-hydroxylase activities per nmol cytochrome P-450 in *C. leptolepis* and *Bathysaurus mollis* were also higher than in control trout. However, both *Antimora rostrata* and *C. rupestris* had values for this character as low as or even lower than those in control trout.

The response of BP-hydroxylase activity in the deep-sea fish to 10^{-4} mol α-naphthoflavone/L is also provided in Table 3. Activity in *C. armatus*, *C. leptolepis*, and *B. mollis* was strongly inhibited, whereas in *C. rupestris* the activity was relatively unaffected, and in *Antimora* the activity was stimulated by α-naphthoflavone. As indicated by the standard deviation, the effect was quite variable in *Antimora*.

The metabolism of aromatic hydrocarbons results in the production of toxic and mutagenic products. The identity of metabolic products may indicate the potential for such toxic effects, and also disclose the preference of cytochrome P-450s for particular sites on a molecule. The profile of metabolites of [^{3}H]−BP produced in vitro by *C. armatus* hepatic microsomes is depicted in Fig. 2. The relative proportions of these metabolites (Table 4) indicate that hepatic cytochrome P-450 metabolizes B[*a*]P with a pronounced regiospecificity, showing a strong preference for the benzo-ring (7,8- and 9,10-diols). Though not indicated in Table 4, from 4 to 8% of the label in metabolites produced here appeared in peaks eluting prior to 9,10-diol.

Discussion

The results presented here establish that microsomal electron transfer components and enzyme activity can be measured in liver samples of fish retrieved from the deep sea. Further, the optical spectra obtained for *Coryphaenoides armatus* hepatic microsomes indicate that some such samples can be obtained with apparently little alteration of the heme environment of cytochrome P-450. However, the suggestion of abundant cytochrome P-420 in other samples implies that degradation of cytochrome P-450 might sometimes be a significant problem in benthic samples. The cause of such degradation is not known. Clearly, it is not strictly related to structural alterations of either cytochrome P-450 or its membrane environment possibly accompanying changes in hydrostatic pressure upon retrieval, as samples retrieved from the greatest depth, *C. armatus* from 3200 m (about 320 atmospheres), gave the best results upon spectrophotometric analysis (e.g. Fig. 1). One might speculate about species differences in stability of the membrane environment of cytochrome P-450 to pressure changes, but it is more likely that some other factor, perhaps related to handling during and after retrieval,

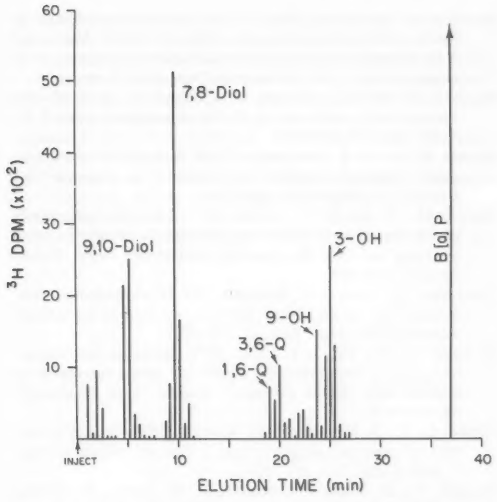

FIG. 2. Elution profile of [^{3}H]benzo[*a*]pyrene metabolites formed by *Coryphaenoides armatus* hepatic microsomes. The sample used for this analysis was the same as that in Fig. 1. Label co-eluting with authentic metabolite standards in analyses of reactions stopped at time 0 was subtracted. Less than 10% of the total substrate was typically metabolized in 20 min. Abbreviations indicated on the chromatogram are: diol; dihydrodihydroxybenzo[*a*]pyrene. Q; benzo[*a*]-pyrene quinone. OH; hydroxybenzo[*a*]pyrene.

effected the appearance of cytochrome P-420.

The inactivation of cytochrome P-450 suggested by the appearance of cytochrome P-420 would contribute to the low monooxygenase specific activity in several of the samples here. However, other factors, such as possible inactivation of cytochrome P-450 by peroxidation of lipid in reaction mixtures could also result in low monooxygenase activity measured in vitro. In rainbow trout liver microsomes lipid peroxidation was not detected (G. Mannering, Univ. of Minnesota, personal communication) but both quality and quantity, and possibly the peroxidation, of lipid could be quite different in the preparations from the deep sea.

The fact that the activities seen in these deep sea samples probably represent minimal values provides emphasis to the findings that both ER *O*-deethylase and BP hydroxylase activities in species from as deep as 3200 m exceeded those often seen in shallow-water species. Moreover, the catalytic efficiency of cytochrome P-450s (activity per nmol P-450) with these substrates in most of the deep-sea samples exceeded that of some untreated shallow water forms. These examples of metabolic capacity and catalytic efficiency in deep sea animals exceeding that in shallow water forms are in contrast to results obtained for overall metabolic rates (Smith 1978) and for activity of some other enzymes. In particular, the M_4 isozyme of lactate dehydrogenase in skeletal muscle of deep sea fishes is present in lesser amounts and has a lower catalytic efficiency than in shallow water species (Childress and Somero 1979; Somero and Siebenaller 1979), although the

TABLE 4. Benzo[*a*]pyrene metabolite formation by hepatic microsomes of *Coryphaenoides armatus*. Values represent the mean obtained with three individual fish. ± values give the range. The concentration of protein in reaction mixtures was 0.4 mg/mL. Typically less than 10% of the total BP in the reaction mixtures was metabolized in the 20-min period. 100% activity was similar to the activity in Table 3.

Metabolite	Percent of total metabolites formed
Prediol[a]	6±2
9,10-dihydrodiol	25±6
4,5-dihydrodiol	<1
7,8-dihydrodiol	35±4
1,6-quinone	3±2
3,6-quinone	4±3
9-hydroxy	7±3
3-hydroxy[a]	20±5

[a]Unidentified metabolites eluting prior to 9,10-dihydro-diol.
[b]Compounds eluting with 3-OH-BP, which can include 1-OH-BP, 3-OH-BP, and 7-OH-BP.

former is not necessarily true of LDHs in heart or brain (Childress and Somero 1979). Such a distinction between cytochrome P-450 and M_4-LDH probably reflects the multiple modes of regulation of cytochrome P-450 isozymes, and a major function of these enzymes in the liver in adaptive processes quite distinct from energy metabolism.

Environmental chemicals are prominent among the factors known to regulate hepatic cytochrome P-450s in fish as well as mammals (for reviews see Bend and James 1978; Lech et al. 1981; Stegeman 1981a). ER *O*-deethylase and BP hydroxylase activities are both carried out preferentially by cytochrome P-450s induced by polynuclear aromatic hydrocarbon-type inducers in fish (Elcombe et al. 1979; Stegeman et al. 1981) and mammals (Burke and Mayer 1974). One or both of these activities per nmol cytochrome P-450 in *C. armatus*, *C. leptolepis*, and *B. mollis* were more like those in experimentally induced rather than in control individuals of another fish species. Moreover, BP hydroxylase activity in these same deep sea species was strongly inhibited by α-naphthoflavone, a finding consistent with previous results for *C. armatus* and *C. leptolepis* from the same vicinity (Stegeman 1981b). Such inhibition is also often linked to cytochrome P-450s induced by PAH, whereas in fish or mammalian hepatic systems lacking PAH-induced hemeproteins BP hydroxylase activity is stimulated or unaffected by ANF (Weibel et al. 1971; Bend et al. 1977; Stegeman et al. 1981). It is significant that BP hydroxylase activity was not inhibited by ANF in those two species with activity per nmol P-450 more like that in control trout.

These results suggest that at least the *C. armatus* sampled here, and possibly *C. leptolepis* and *B. mollis*, could be reflecting exposure to biochemically significant levels of compounds active as PAH-type inducers of cytochrome P-450. However, the origin of these characteristics suggesting

induction is unclear. As discussed recently (Stegeman 1981a) certain natural products might be responsible for such induction. But the benthic habitat, feeding in the sediment (McClellan 1976) where organic contaminants are likely to be most concentrated, and the position of capture off the eastern seaboard of North America, make the possibility of exposure to anthropogenic pollutants also quite likely. There is evidence that hepatic monooxygenase systems in many coastal fish in some regions have been induced by environmental chemicals (Bend et al. 1979; Stegeman et al. 1981). But much like the situation with the coastal scup, *Stenotomus chrysops*, (Stegeman et al. 1981), there is a need to obtain a sample of *C. armatus*, and of *C. leptolepis* and *B. mollis*, lacking characteristics of induced fish, to substantiate the speculation that the individuals examined here had been induced and that these characteristics are not inherent. If further evidence supporting induction can be obtained, including tissue residues of likely inducers, then it would be very interesting to determine the geographic ranges over which animals possessing features associated with induced cytochromes P-450 are distributed in the deep sea.

The regiospecificity of BP metabolism by *C. armatus* hepatic microsomes, with a strong preference for metabolism on the benzo-ring, is also a characteristic of PAH-induced cytochromes P-450s, at least in mammals (Holder et al. 1974). However, such regiospecificity seems to be typical of teleost hepatic cytochrome P-450s, whether from induced or control fish (Stegeman 1981a). Nevertheless, this pattern of metabolism associated with production of mutagenic derivatives could have important implications for the health of animals exposed to PAH in the deep sea.

Although the data clearly indicate that hepatic microsomal enzymes in deep sea fish are similar to those in shallow water forms, the limitations on these data preclude an estimate of the total in vitro capacity for biotransformation of hydrocarbons, with the possible exception of the deepest samples, *C. armatus*. Further studies considering variables that might affect the integrity and catalytic function of microsomal systems in fish from the deep sea are necessary to achieve such estimates. Among these variables, a study of the influence of pressure on monooxygenase systems might not only improve our estimates of biotransformation capacity, but also provide information on structural and functional adaptations of membrane-bound enzymes in deep sea animals.

Acknowledgments

This work was supported by National Science Foundation (U.S.) grant OCE80-18569. I wish to thank Drs George Somero, Joseph Siebenaller, Richard Haedrich and Eugene Copeland for their assistance in obtaining the deep sea samples used here. I am also grateful to Bruce R. Woodin, who provided expert technical assistance in this work. Drs Russell Cuhel, John Bend, and Holger Jannasch made useful comments on the manuscript. Contribution Number 5037 from the Woods Hole Oceanographic Institution.

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Microbial and Photochemical Degradation of Polycyclic Aromatic Hydrocarbons in Estuarine Waters and Sediments[1]

RICHARD F. LEE AND CHARLOTTE RYAN

Skidaway Institute of Oceanography, P.O. Box 13687, Savannah, GA 31406, USA

LEE, R. F., AND C. RYAN. 1983. Microbial and photochemical degradation of polycyclic aromatic hydrocarbons in estuarine waters and sediments. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 86–94.

Radiolabeled polycyclic aromatic hydrocarbons (PAH) containing up to three rings, including naphthalene, methylnaphthalenes, and phenanthrene, were degraded (measured by $^{14}CO_2$ production) in water samples from both Narragansett Bay and southeastern United States. Higher weight PAH, including benz[*a*]anthracene, chrysene, fluorene, and anthracene, showed little, if any, degradation in water but were readily degraded when added to sediment–water slurries. In areas with low levels of petroleum in the water or sediment there was a lag before appreciable degradation began, and the rate of degradation fitted a first-order equation. Half-lives, calculated for the various PAH added to water or sediment–water slurries, were very low during winter months; [^{14}C]methylnaphthalene added to water from Skidaway River, Georgia, in January (8°C) was 57 d, while in September (28°C) it was 3 d. PAH added to sediments or water from oil-treated areas or mesocosms were rapidly degraded with no lag phase and the degradation rate was linear. [^{14}C]Methylnaphthalene added to water from control and oiled mesocosms in May (10°C) had half-lives of 300 and 5 d, respectively. We plotted the changes in turnover times with changes in the concentration of PAH and calculated the natural turnover times and V_{max} for PAH added to water or sediment from the oiled mesocosms. When [^{14}C]dimethylbenz[*a*]anthracene was incubated in water in the dark no degradation occurred, but when exposed to sunlight, 0.3% was mineralized in 18 h. In addition, a variety of photooxidation products were produced. The production of $^{14}CO_2$ in the light was due to microbial degradation of photooxidation products of [^{14}C]dimethylbenz[*a*]anthracene.

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On a laissé se dégrader (tel qu'indiqué par production de $^{14}CO_2$) des hydrocarbures aromatiques polycycliques (PAH) marqués par isotope radioactif et contenant jusqu'à trois noyaux, y compris le naphthalène, les méthylnaphthalènes et le phénanthrène, dans des échantillons d'eau de la baie de Narragansett et du sud-est des États-Unis. Les PAH de poids moléculaire élevé, dont le benz[*a*]anthracène, le chrysène, le fluorène et l'anthracène, ne se dégradent que très peu dans l'eau, si tant est qu'il y a dégradation. Par contre, ils se dégradent facilement lorsque ajoutés à des boues de sédiment–eau. Dans les endroits où les niveaux de pétrole dans l'eau sont peu élevés, il y a dégradation appréciable avec décalage, et le taux de dégradation s'exprime par une équation de premier ordre. Les demi-vies des divers PAH ajoutés à l'eau ou aux boues de sédiment–eau sont très courtes en hiver; celle du [^{14}C]méthylnaphthalène ajouté à de l'eau de la rivière Skidaway (Géorgie) en janvier (8°C) est de 57 jours, alors qu'en septembre (28°C) elle est de 3 jours. Les PAH ajoutés aux sédiments ou à l'eau de zones ou microcosmes traités au pétrole se dégradent rapidement, sans décalage, à un taux linéaire. Le [^{14}C]méthylnaphthalène ajouté à l'eau témoin et aux microcosmes traités au pétrole en mai (10°C) a des demi-vies de 300 et 5 jours respectivement. Nous avons porté sur graphique les changements de temps de renouvellement en fonction des changements de concentration des PAH et calculé le temps de renouvellement naturel ainsi que le V_{max} pour les PAH ajoutés à l'eau ou aux sédiments de microcosmes traités au pétrole. Si l'on incube le [^{14}C]méthylbenz[*a*]anthracène dans de l'eau à l'obscurité, il ne se produit aucune dégradation, mais à la lumière solaire, 0,3 % est minéralisé en 18 h.

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6851)
Imprimé au Canada (J6851)

Il y a en outre production de divers produits de photo-oxydation. La production de $^{14}CO_2$ à la lumière est due à une dégradation microbienne des produits de photo-oxydation de [^{14}C]diméthylbenz[*a*]anthracène.

Received March 18, 1982
Accepted December 20, 1982

Reçu le 18 mars 1982
Accepté le 20 décembre 1982

As a result of man's activities high concentrations of polycyclic aromatic hydrocarbons (PAH) are often found in coastal waters and sediments near urban areas. A variety of physical, chemical, and biological processes affect the fate of PAH (Farrington and Meyers 1975; Lee 1980). This report deals with the microbial and photochemical degradation of radiolabeled PAH added to estuarine sediments and waters from the southeastern and northeastern coasts of the United States.

Microbes able to metabolize PAH to various oxygenated derivatives with eventual degradation to CO_2 have been isolated from aquatic environments (Gibson 1976). Our studies focused on the rate of mineralization (production of $^{14}CO_2$) of radiolabeled PAH added to sediment or water samples. This technique, often referred to as hydrocarbon degradation potential, has been used by a number of investigators to study hydrocarbon degradation in natural waters and sediment (Atlas 1979; Caparello and LaRock 1975; Hodson et al. 1977; Lee 1977; Robertson et al. 1973; Seki 1976; Walker and Colwell 1976a). Factors that effect the degradation kinetics of PAH include the following: (1) most "clean" areas have a very low number of PAH-degrading bacteria relative to the number of microbes able to degrade amino acids or similar soluble organics (Atlas 1981); (2) low solubility of PAH in water and a tendency to absorb to living and dead suspended particles (Herbes 1977; Lee 1980; Mackay and Shiu 1977); (3) inhibition of marine microbial activity by high concentration of hydrocarbons (Colwell and Walker 1977; Hodson et al. 1977).

The microbial degradation of soluble organic compounds, primarily glucose and amino acids, in aquatic environments has been extensively investigated using ^{14}C-labeled compounds (Parsons and Strickland 1962; Vaccaro and Jannasch 1966; Williams and Askew 1966; Wright and Hobbie 1965). This work has provided insight into heterotrophic processes occurring in natural waters. In some natural waters, [^{14}C]-glucose mineralization rates increase hyperbolically with increases in glucose concentration and can be described by the modified Lineweaver–Burk equation discussed by Wright and Hobbie (1966). One of our goals was to determine if such Michaelis–Menten kinetics were applicable to the mineralization of PAH.

In addition to microbial degradation, PAH are susceptible to photooxidation in seawater (Larson et al. 1976). In experiments reported here, microbial degradation was allowed to occur in water exposed to sunlight in order to determine the amount of degradation when both photooxidation and microbial degradation act together on PAH.

Materials and Methods

The sites in the southeast were near Savannah, GA, and a heavily oiled area near Charleston, SC. Water and sediment from Narragansett Bay, RI, were contained in mesocosms, some of which were treated with fuel oil with others serving as controls. The high hydrocarbon concentrations in a heavily oiled portion of the Cooper River near Charleston have been reported by Lee (1977); hydrocarbon concentrations, salinity, and temperatures for the Skidaway River, an estuarine river near Savannah, by Lee (1977) and Lee and Ryan (1976); mesocosms in use at the Marine Ecosystem Research Laboratory at the University of Rhode Island by Pilson et al. (1979). Changes in hydrocarbon concentrations in water and sediment after fuel oil was added to the mesocosms have been reported by Gearing et al. (1979) and Wade and Quinn (1980).

To determine microbial degradation of PAH in water, ^{14}C-labeled compounds were added to 100-mL water samples in 250-mL flasks capped with silicon stoppers. After incubation at in situ temperature, 0.2 mL of 2 *M* H_2SO_4 was added to the water, and the respired $^{14}CO_2$ was collected in a center well containing a piece of Whatman No. 1 filter paper soaked with 0.4 mL of 2 *M* NaOH. After absorption of the $^{14}CO_2$ by the NaOH for 3 h, the soaked papers were transferred to a second set of flasks equipped with $^{14}CO_2$ traps containing phenethylamine (New England Nuclear). One millilitre of 2 *M* H_2SO_4 was added to each flask, and after 3 h the $^{14}CO_2$ in the phenethylamine-soaked paper was transferred to scintillation vials and counted in a liquid scintillation counter. The two steps for collection of $^{14}CO_2$ were necessary because a small amount of the ^{14}C-labeled compounds volatilized and was collected in the NaOH trap. Controls were water samples containing mercuric chloride at a concentration of 10 mg/L. All samples were in triplicate for each concentration and time interval.

Microbial degradation of PAH in sediment was determined by adding ^{14}C-labeled compounds to sediment–seawater slurries (1 g of sediment and 50 mL of seawater in 125-mL bottles capped with silicon stoppers). Controls were bottles containing mercuric chloride at a concentration of 10 mg/g sediment. At the end of the various incubation periods $^{14}CO_2$ was collected and counted as described above. When saturation kinetics were assumed, the mineralization data were fitted to the Lineweaver–Burk equation discussed by Wright and Hobbie (1966) for glucose:

$$t/f = \frac{K + S}{V_{max}} + \frac{A}{V_{max}}$$

where t = time of incubation, f = fraction of [^{14}C]glucose which is mineralized to $^{14}CO_2$, K = an uptake constant, S = natural glucose concentration, V_{max} = maximum glucose mineralization potential, and A = concentration of added glucose. The turnover expression, t/f, is the time required for complete mineralization of the compound. Least-square

TABLE 1. Potential degradation of radiolabeled polycyclic aromatic hydrocarbons added to water or sediment from oil-treated and untreated mesocosms in Rhode Island.

Hydrocarbon	Added to:	PAH concentration (μg/L for water and μg/g for sediment)	Oil treatment[a]	Month	Temperature (°C)	Calculated half-life (d)
Naphthalene	Water	10	None	May	10	125
		25	None	May	10	300
		50	None	May	10	320
		10	Yes	May	10	4
		25	Yes	May	10	5
		50	Yes	May	10	7
		25	None	August	23	20
2-Methylnaphthalene	Water	10	None	April	7	390
		25	None	April	7	530
		10	Yes	April	7	12
		25	Yes	April	7	17
		50	Yes	April	7	30
		25	None	August	23	53
		25	Yes[b]	August	23	40
		25	Yes	August	23	2
		25	Yes	May	10	2
Phenanthrene	Water	25	None	January	2	11 000
		25	None	December	8	180
		25	None	June	18	79
Anthracene	Sediment	1.0	None	June	18	95
		2.5	None	June	18	99
		5.0	None	June	18	141
		1.0	Yes	June	18	5
		2.5	Yes	June	18	6
		5.0	Yes	June	18	7
Benz[*a*]anthracene	Sediment	2.5	None	February	4	21 000
		2.5	None	May	8	2 400
		2.5	None	October	15	1 100
		1.0	Yes	June	18	6
		2.5	Yes	June	18	6
		5.0	Yes	June	18	8
Fluorene	Sediment	1.0	None	May	10	37
		1.0	Yes	May	10	11
		2.5	Yes	May	10	20
		5.0	Yes	May	10	28
Chrysene	Sediment	2.5	None	August	23	510
		2.5	Yes	August	23	190

[a]The treated mesocosm had fuel oil added as described by Gearing et al. (1979).
[b]Fuel oil addition was stopped 2 wk prior to the date when radiolabeled methylnaphthalene was added to this water sample.

linear regression analysis of t/f against A can be used to calculate V_{max} and h, the intercept on the t/f axis ($A = 0$), which represents the turnover time of natural glucose in the water sample. Using this equation, where the hydrocarbon is substituted for glucose, the natural turnover time is calculated for the hydrocarbon under study, i.e. the turnover time for the hydrocarbon in the water before the addition of the radiolabeled hydrocarbon.

Radiolabeled compounds used included 2-[8-^{14}C]methylnaphthalene (136.9 MBq/mmol) (California Bionuclear Corp.), 1-[^{14}C]naphthalene (135.8 MBq/mmol) (Amersham), [9-^{14}C]fluorene (95.1 MBq/mmol) (California Bionuclear Corp.), 9-[^{14}C]anthracene (76.6 MBq/mmol) (California Bionuclear Corp.), 9-[^{14}C]phenanthrene (418.1 MBq/mmol) (Amersham), 12-[^{14}C]benz[*a*]anthracene (1776 MBq/mmol) (Amersham), 3,4-[*benz*-3,6-^{14}C]pyrene (777 MBq/mmol) (Amersham), 5,6-[11,12-^{14}C]chrysene (233.1 MBq/mmol) (Amersham), 7,12-dimethyl[12-^{14}C]benz[*a*]anthracene (777 MBq/mmol) (Amersham), and [7-^{14}C]dibenz[*a*,*h*]anthracene (445.5 MBq/mmol) (Amersham).

For photochemical studies radiolabeled compounds were added to 100 mL of water in 250-mL quartz flasks (Quartz Products) which allowed 100% transmission of light with wavelengths longer than 200 nm. The quartz flasks were suspended in an outside tank through which estuarine water flowed. Dark controls were flasks covered with aluminum foil, while chemical controls were flasks with mercuric chloride. The amount of $^{14}CO_2$ produced during the incubation was determined as described above. In addition to collecting $^{14}CO_2$, other organic metabolites were collected by extraction of the water with chloroform. Extracts were run on a high-pressure liquid chromatograph (Micrometrics) equipped with ultraviolet and fluorescence detectors. The column was a 25-cm Whatman Partisil PSX-10 ODS-2. The solvent system

TABLE 2. Potential degradation rate of PAH added to water or sediment from estuarine areas of Charleston, SC, and Savannah, GA. The concentration of radiolabeled hydrocarbon in each sample tested was 25 μg/L water or 2.5 μg/g sediment.

Hydrocarbon	Added to:	Site	Month	Temperature (°C)	Calculated half-life (d)
Naphthalene	Water	GA	January	8	180
		GA	April	15	7
		GA	October	26	2
		SC	June	22	14
2-Methylnaphthalene	Water	GA	January	8	57
		GA	April	15	41
		GA	May	18	12
		GA	June	24	7
		GA	September	28	3
		GA	October	26	3
		SC	June	22	16
		SC	August	27	13
Phenanthrene	Water	GA	January	8	210
		GA	August	27	19
		GA	September	28	24
		SC	August	27	36
Fluorene	Sediment	GA	May	18	180
		GA	August	28	82
Anthracene	Sediment	GA	August	28	210
		SC	August	27	57
Benz[*a*]anthracene	Sediment	GA	January	8	470
		GA	April	15	340
		GA	August	28	120
		SC	August	27	16
Chrysene	Sediment	GA	January	8	1400
		GA	August	28	246
		SC	August	27	79

was isocratic with 72.5% methanol in water. After passing through a fluorescence detector, 0.5-mL samples were counted with a scintillation counter.

Results

MICROBIAL DEGRADATION

Polycyclic aromatic hydrocarbons (PAH) containing up to three rings, including naphthalene, methylnaphthalene, and phenanthrene, were degraded in water samples from both Narragansett Bay and southeastern United States (Tables 1 and 2). Higher weight PAH, including benz[*a*]anthracene, chrysene, fluorene, and anthracene, showed little, if any, degradation in water samples but were readily degraded when added to sediment–water slurries (Tables 1 and 2). Higher weight PAH, including benzo[*a*]pyrene, dimethylbenz[*a*]-anthracene, and dibenz[*a*,*h*]anthracene, showed degradation only slightly above detection limits in sediment–water slurries.

In areas unaffected by petroleum there was a lag before appreciable mineralization occurred (Fig. 1 and 2), and degradation could be expressed by the first-order equation

$$dc/dt = kc$$

where k is the rate constant and c is the concentration of the compound at time t. For example, a semilog plot of [^{14}C]-phenanthrene degradation with time in water from a control mesocosm at 18°C gave a straight line expressed by the equation $\ln c = 2.33 - 0.000363t$ (Fig. 1). The calculated half-life, the time for 50% of the [^{14}C]phenanthrene to be degraded to $^{14}CO_2$, was 79 d. In all study areas the rates of degradation were slower (longer half-lives) in the colder months (Tables 1 and 2). Thus, the half-lives for methylnaphthalene in water from the Skidaway River, GA, decreased from 57 to 3 d going from January (8°C) to September (28°C) (Fig. 3; Table 2). The half-lives for phenanthrene added to water from Narragansett Bay decreased from 11 000 to 79 d from January (2°C) to June (18°C) (Table 1). Higher weight PAH in sediment samples were also degraded at much slower rates in the winter (Fig. 4 and 5).

As expected, degradation of radiolabeled PAH added to sediment and water from oiled areas were much higher than those from "cleaner" sites. There was little or no lag in the degradation of PAH added to oiled sediment or water (Fig. 4 and 5). The half-life of benz[*a*]anthracene in sediment from a heavily oiled area near Charleston and a "cleaner" site near Savannah were 16 and 120 d, respectively (Table 2; Fig. 5). Similar differences in the degradation rates were noted for anthracene and chrysene (Table 2). The degradation of radiolabeled PAH added to sediment or water from oiled areas was linear as shown for the degradation of benz[*a*]anthracene in sediment from an oiled mesocosm (Fig. 4). Much shorter

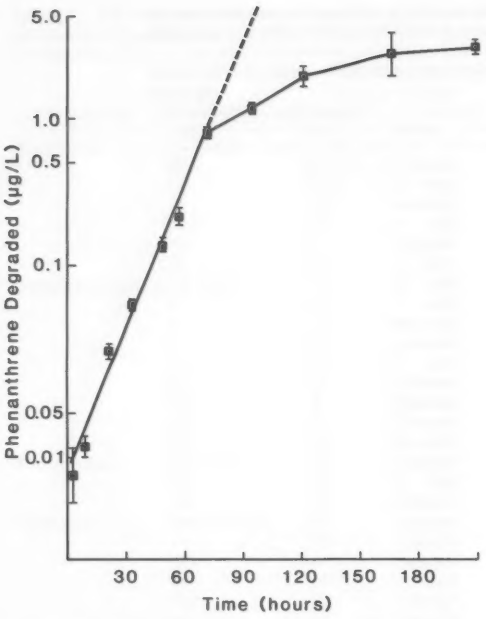

FIG. 1. Degradation of [^{14}C]phenanthrene in water (initial concentration, c_0, of 25 µg/L) from a controlled mesocosm. Mesocosm and incubation temperature was 18°C. The equation for phenanthrene degradation can be expressed by $\ln c = 2.33 - 0.000363t$ ($r = 0.90$, $n = 7$) where c is the concentration of phenanthrene at time t. Vertical bars represent standard deviations with $n = 4$.

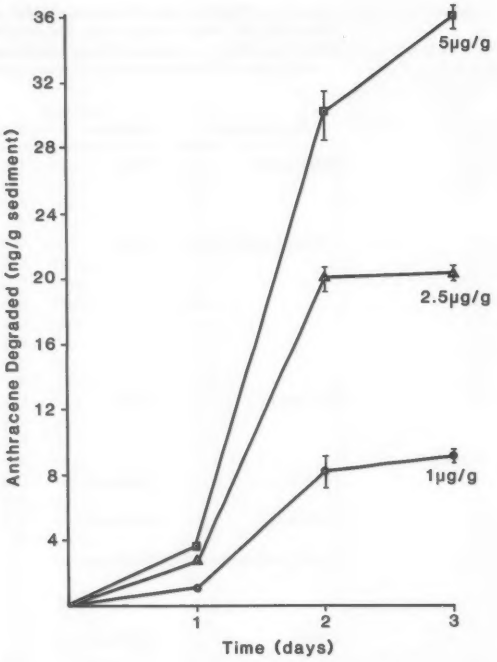

FIG. 2. Degradation of various concentrations of [^{14}C]anthracene added to sediment samples from a control mesocosm. Mesocosm and incubation temperature was 18°C.

half-lives were found for radiolabeled PAH added to water from oiled mesocosms relative to control mesocosms. For example, half-lives of [^{14}C]methylnaphthalene added to water from a control and oiled mesocosm in August were 53 and 2 d, respectively (Table 1). Two weeks after fuel oil addition was stopped in August the half-life of methylnaphthalene had increased to 40 d in the previously oiled mesocosm (Table 1).

Increases in hydrocarbon concentrations resulted in corresponding increases in the rate of hydrocarbon degradation (Fig. 2 and 4). Whether saturation (Michaelis–Menton) kinetics are obeyed is not clear, since at higher concentrations (e.g. above 100 µg/L for water samples) there was a decrease in the rate of hydrocarbon degradation, presumably because of hydrocarbon inhibition of microbial activity. The changes in turnover time, t/f, with benz[a]anthracene concentrations, assuming that saturation kinetics were obeyed, are shown in Fig. 6. Turnover time is the time required to convert all hydrocarbon to $^{14}CO_2$. The modified Lineweaver–Burk equation of Wright and Hobbie (1966) was used to calculate the natural turnover time for the hydrocarbon in the water or sediment before addition of the radiolabeled hydrocarbon. As calculated in Fig. 6, the natural turnover time for benz[a]-anthracene in an oil-treated microcosm was 10 d in June. Thus, benz[a]anthracene in this fuel oil treated microcosm should be completely mineralized by microbes in 10 d. In colder periods the turnover times were much lower so that the calculated natural turnover time for methylnaphthalene in April (7°C) was 20 d (Table 3) compared with 7 d for naphthalene in May (10°C). At the same temperature, methylnaphthalene and naphthalene in oiled microcosms had very similar degradation rates (Table 1). The inverse of the slope of the line gives V_{max}, which for benz[a]anthracene in June was 0.60 µg/d. For the calculations to be valid, the mineralization rate must be constant throughout the incubation at each hydrocarbon concentration. This occurred only in water or sediment from areas previously treated with oil (compare Fig. 2 and 5).There was an initial lag period, and the mineralization rate was first-order in water or sediment from areas not previously treated with oil.

PHOTOCHEMICAL AND MICROBIAL DEGRADATION

Experiments were carried out to study photochemical oxidation in combination with microbial degradation of PAH. All of the [^{14}C]dimethylbenz[a]anthracene was recovered when incubated in the dark with no $^{14}CO_2$ produced. However, when exposed to sunlight, 0.3% was mineralized in 18 h. A number of degradation products, in addition to $^{14}CO_2$, were observed when an extract of a water sample exposed to

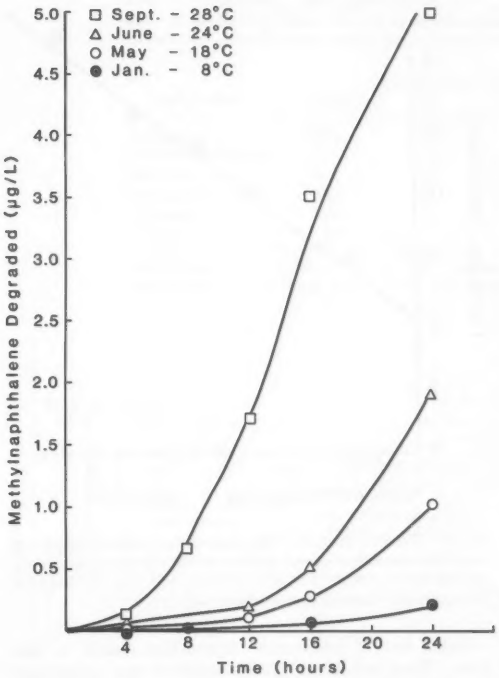

FIG. 3. Degradation of [^{14}C]methylnaphthalene added to water samples (initial concentration, c_0, of 25 µg/L) from the Skidaway River, GA. Each point is the amount of degradation run in triplicate. The degradation rate equation for September is $\ln c = 3.27 - 0.0115t$ ($r = 0.99$) where c is the concentration at time t. For June, the equation is $\ln c = 3.23 - 0.00301t$ ($r = 0.91$) and for May, $\ln c = 3.23 - 0.00196t$ ($r = 0.92$).

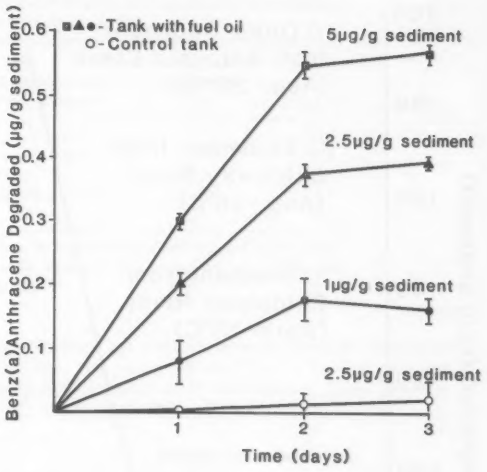

FIG. 4. Degradation of [^{14}C]benz[*a*]anthracene added to sediment samples from oiled and control mesocosms. Mesocosm and incubation temperature was 18°C.

sunlight was analyzed by high-performance liquid chromatography (Fig. 7). One compound identified by comparison of the retention time with an authentic standard was benz[*a*]anthracene-7,12-dione. This compound was previously reported as a photooxidation product of 7,12-dimethylbenz[*a*]anthracene (Wood et al. 1979). Other photooxidation products came off the liquid chromatograph with retention times similar to phenols and diols. Benz[*a*]anthracene, anthracene, and benzo[*a*]pyrene were not mineralized in the dark water samples but were degraded to $^{14}CO_2$ when exposed to sunlight (data not presented). Also, a number of photooxidation products were formed, including ketones, diones, and quinones (e.g. anthrone from anthracene).

Discussion

Addition of radiolabeled hydrocarbons to sediment or water from a "clean" site resulted in a pronounced lag before degradation commenced. Other researchers have noted similar lags when [^{14}C]hexadecane was added to natural water (Walker and Colwell 1976b; Ward and Brock 1976). The hydrocarbon degradation curves observed in control mesocosms or other "clean" waters or sediments (Fig. 2–4) resembled typical log growth curves for "normal" and petroleum-degrading bacteria (Pelczar and Reid 1965; Jobson et al. 1972; Mulkins-Phillips and Stewart 1974). We suggest that these samples initially had low numbers of hydrocarbon-degrading microbes in the water or sediment and growth of these microbes began after radiolabeled PAH were added. Most studies have shown that marine areas with a low petroleum content have only small numbers of petroleum-degrading microbes (Atlas 1981; Colwell et al. 1976).

Our work showed high linear rates of degradation when radiolabeled PAH were added to sediments or water with previous petroleum input. Presumably, the addition of petroleum allowed for increased growth of petroleum-degrading microbes which were in the log phase of growth when radiolabeled PAH were added. We suggest that the addition of petroleum, acting as an important source of carbon, resulted in a few species becoming the dominant microbes. Thus, microbes in areas with a high petroleum input would behave as a monoculture. Hydrocarbon-degrading microbes in pure cultures show linear rates of hydrocarbon degradation (Gibson 1975; Liu and Wong 1976; Walker et al. 1973). Typically, when microbiology studies are carried out after adding petroleum to a marine area, large numbers of petroleum-degrading microbes are isolated from the site (Pierce et al. 1975).

Temperature and the concentration of inorganic nutrients (nitrogen and phosphorus) are among the factors which affect the rate of petroleum biodegradation. Lower numbers of hydrocarbon-degrading bacteria were found in Raritan Bay, NJ, in winter relative to other times of the year (Atlas and Bartha 1973). Our studies indicated that potential PAH

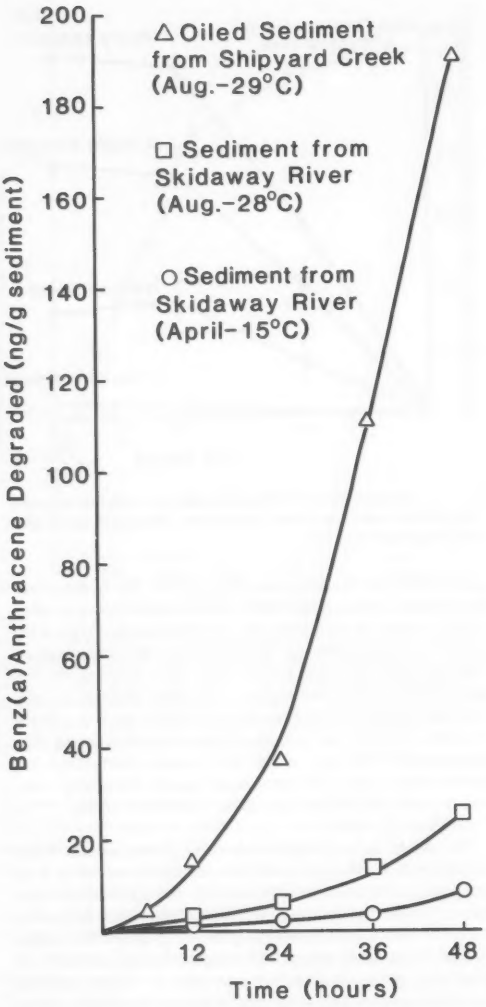

FIG. 5. Degradation of [^{14}C]benz[*a*]anthracene added to sediment from Skidaway River, GA, and Shipyard Creek, SC. The Shipyard Creek station was near Charleston, SC, where the sediment had a very high petroleum content.

degradation rates were very low during colder months in both sediment and water from both Narragansett Bay and the Skidaway River. Heterotrophic activity, as determined by glucose mineralization, in aquatic environments showed highest activity in summer and lowest values in the winter (Goulder 1980). High summer activity was presumably due to both a higher density of bacteria and to higher metabolic activity of individual bacteria at the higher temperatures.

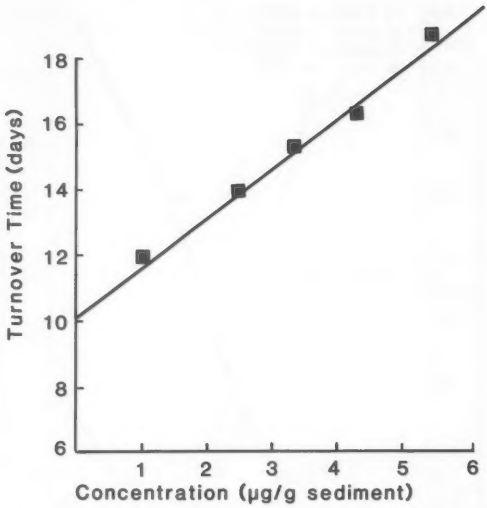

FIG. 6. Turnover times of [^{14}]benz[*a*]anthracene added to sediment samples from a fuel oil treated mesocosm. The equation of the regression line is $t/f = 10.0 + 1.67\,c$ ($r = 0.98$, $n = 5$). $V_{max} = 0.60$ µg/d. Mesocosm and incubation temperature was 18°C.

Based on [^{14}C]hexadecane degradation studies in lake water, Ward and Brock (1976) suggested that temperature controlled hydrocarbon degradation in winter and inorganic nutrients limited that rate in summer. Studies on the effects of temperature and nutrients on microbial degradation of hydrocarbons have been reviewed by Atlas (1981) and Colwell and Walker (1977). Taking lowered degradation rates in winter into account, the degradation of naphthalene and methylnaphthalenes in an oil-treated mesocosm was 1.4 and 1.9 $mg \cdot L^{-1} \cdot yr^{-1}$, respectively.

Our sediment samples were taken from the upper 1 cm where microbial degradation of hydrocarbon is highest (Gardner et al. 1979; Ward et al. 1980). The calculated turnover times of fluorene, benz[*a*]anthracene, and anthracene in oil-treated sediment were 12, 10, and 7 d, respectively (Table 3). These calculations are true only if the hydrocarbons remain in the surface sediment (i.e. at the water–sediment interface). Actually, hydrocarbons enter subsurface sediments by bioturbation and other mixing processes (Hinga et al. 1980; Lee et al. 1982). Microbial activity in subsurface sediments is low, and hydrocarbons a few centimetres below the surface can remain unmodified for years (Gardner et al. 1979; Gearing et al. 1980; Hughes and McKenzie 1975; Ward et al. 1980). In marine areas exposed to oil, mixed communities of hydrocarbon-degrading microbes develop which are able to metabolize both aliphatic and aromatic hydrocarbons with rapid degradation of alkanes and slower attack on isoalkanes, cycloalkanes, and aromatic hydrocarbons (Atlas 1981; Blumer et al. 1973). Our experiments indicate that surface sediments of oiled areas are able to rapidly degrade many PAH.

TABLE 3. Calculated natural turnover times and V_{max} for radiolabeled polycyclic aromatic hydrocarbons added to sediment or water from oil-treated mesocosms from Rhode Island.

Hydrocarbon	Month	Temperature (°C)	Hydrocarbon concn. before addition[a]	Calculated natural turnover time (d)	V_{max} (μg/d)
Naphthalene	May	10	1.5 μg/L water	7	10.3
2-Methylnaphthalene	April	7	1.4 μg/L water	20	5.3
Fluorene	May	10	ND	12	0.1
Benz[*a*]anthracene	June	18	0.3 μg/g sediment	10	0.6
Anthracene	June	18	ND	7	0.5

[a]Concentration of the compound in the sediment or water before addition of radiolabeled hydrocarbon. Naphthalene and methylnaphthalene concentrations were reported in Gearing et al. (1979) and benz[*a*]anthracene in Hinga et al. (1980). ND, not determined.

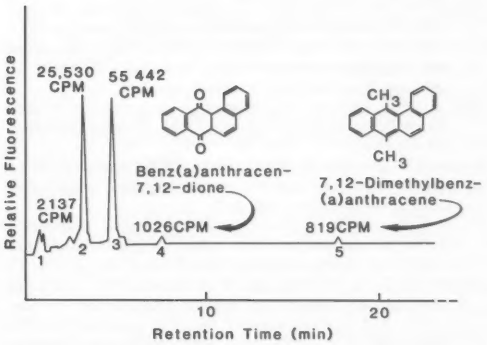

FIG. 7. High-performance liquid chromatogram of the photochemical oxidation of products of dimethylbenz[*a*]anthracene. 7,12-Dimethyl[12-^{14}C]benz[*a*]anthracene was added to water samples to give a final concentration of 10 μg/L and was suspended in a quartz flask in the upper 3 cm of a control mesocosm in August (23°C). After 4 h, an extract was analyzed using a high-performance liquid chromatograph. Peaks 2 and 3 have retention times similar to authentic monohydroxylated derivatives of dimethylbenz[*a*]anthracene. Peak 4 had an identical retention time to benz[*a*]anthracene-7,12-dione. Peak 5 is dimethylbenz[*a*]anthracene. CPM, counts per minute.

Ultraviolet light is not as important in degrading PAH in water as in air, since short wavelengths, including those in the visible region, do not penetrate far below the surface in natural waters. Higher molecular weight PAH (e.g. benzo[*a*]-pyrene) are degraded by light with wavelengths longer than 300 nm and can be completely photooxidized in seawater within a few hours after exposure to sunlight (Andelman and Suess 1970). The principal products of photooxidation of dimethylbenz[*a*]anthracene in aqueous solution are monohydroxy derivatives and diones (Wood et al. 1979). Benz-[*a*]anthracene-7,12-dione was one of the photooxidation products identified in our experiment with 7,12-dimethyl-[12-^{14}C]benz[*a*]anthracene. The production of $^{14}CO_2$ from this radiolabeled hydrocarbon was not directly due to photooxidation, since when a sunlight water sample containing 7,12-dimethyl[12-^{14}C]benz[*a*]anthracene was poisoned with mercury, no $^{14}CO_2$ was produced during a 2-d incubation period. Since the parent compound cannot be mineralized in the dark, the production of $^{14}CO_2$ in the light was due to microbial degradation of the photooxidation products of 7,12-dimethyl[12-^{14}C]benz[*a*]anthracene.

Acknowledgments

This work was supported by U.S. Environmental Protection Agency grant R 80607202 to the University of Rhode Island and by the Georgia Sea Grant Program, supported by NOAA Office of Sea Grants, U.S. Department of Commerce, under grant NA 80AA-D-00091.

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Session I — Summary and Overview: Fossil Fuel Hydrocarbons

JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

AND JOHN W. FARRINGTON

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

Previous assessments had identified urban inputs as a large fraction of the total fossil fuel input to the marine environment. However, exact sources of inputs and relative contributions within the urban area were not well known. Hoffman et al. conducted a very significant study of the inputs from different types of land use for some urban areas on the shore of Narragansett Bay, Rhode Island. By measuring hydrocarbons in storm drains before, during, and after storms and calculating loadings for different amounts of rainfall, they were able to demonstrate that industrial and interstate highway uses gave the highest fluxes of petroleum hydrocarbons. Commercial and residential land uses — in that order — provided the next highest fluxes. By using compilations of land use patterns, it was possible to calculate total flux to Narragansett Bay. It seems reasonable to presume that these results are indicative of the situation in other similar urban areas.

While significant progress has been made in understanding fluxes of hydrocarbons to estuaries from urban areas, the questions of the flux of fossil fuel compounds from estuaries to continental shelf areas is at an early stage of investigation. Wade et al. combined hydrocarbon and coprostanol (mammalian fecal sterol) measurements of over 80 particulate matter samples taken near the mouth of Chesapeake Bay in an attempt to document the flux of fossil fuel compounds from the bay to the shelf. Despite the incorporation of salinity data and a general understanding of outwelling of Chesapeake Bay water to the shelf into their interpretations, it was difficult to ascertain whether the particulate matter fossil fuel compounds were from the bay or already present as pelagic tar in the shelf waters. The influence of the complicated dynamics of coastal frontal systems on particulate matter distributions obscures any definitive gradients from the mouth of the bay to the shelf areas. However, the detection of particulate coprostanol indicates that some fraction of the particulate matter organic compounds probably originated within Chesapeake Bay. The study by Wade et al. clearly illustrates the importance of a better understanding of physical dynamics in coastal areas as a key factor in advancing our knowledge of the biogeochemistry of pollutants in coastal areas.

Five papers addressed various key processes in biogeochemical cycles of fossil fuel pollutants. Laboratory experiments by Leversee et al. drew attention to the importance of association of polycyclic aromatic hydrocarbons (PAH) with humic materials as a controlling factor in bioavailability and accumulation of PAH in biota and in the physical–chemical behavior of PAH during transit from fresh to saline waters. The experiments utilized six PAH and clearly demonstrated that differences in structure, e.g. benzo[*a*]-pyrene compared with methylcholanthrene, could have a marked influence on the interactions between humic materials, PAH with respect to bioavailability, and salinity-induced coprecipitation. These results, and results of studies by other scientists cited by Leversee et al., document the importance of humic material–fossil fuel compound interactions as a probable flux control mechanism, as both types of compounds transit from freshwater through estuaries to shelf waters.

Gearing and Gearing present interesting data on the influence of storm-resuspended sediment on removal of hydrocarbons from estuarine waters as experimentally investigated in the MERL microcosms. The simulated storm event caused no major differences in the overall fate of several different hydrocarbons added to the microcosms as compared

Printed in Canada (J7253)
Imprimé au Canada (J7253)

with control systems operated without a simulated storm event. The authors hypothesize that the dominant particulate phase responsible for transfer of hydrocarbons from the water column to the sediment is organic carbon rich living or detrital particles, rather than resuspended sediments. A brief discussion of several previously published MERL hydrocarbon and No. 2 fuel oil experiments reviewed major findings and the utility of microcosms in research concerned with biogeochemical processes.

The experiments on microbial and photochemical degradation of PAH in estuarine waters and sediments reported by Lee and Ryan produced several interesting results. Heavier molecular weight PAH, including benz[*a*]anthracene, chrysene, fluorene, and anthracene, showed little, if any, degradation in water. However, addition of a sediment–water slurry promoted degradation. Further evidence was presented for a lag period before degradation at appreciable rates occurs in relatively petroleum-free systems, while no lag period is apparent for systems that have been exposed to significant oil inputs — a phenomenon now well documented. Perhaps the most interesting result concerned experiments with ^{14}C-labeled dimethylbenzanthracene. Incubations in the dark showed no degradation, while incubations in sunlight showed degradation. A variety of photochemical products were produced and some were evidently degraded to CO_2 by microbes. This interesting area of research — interactions between photochemical reactions and biochemical reactions to alter and degrade petroleum compounds — is certain to be expanded in the future, as it is of obvious importance to a more complete understanding of the fate of fossil fuel compounds.

The influence of the depth of mixing of oil into sediments on the long-term fate and longevity of contamination has been well documented in field studies. Anderson et al.'s controlled experiments in an intertidal environment over a year added further evidence that petroleum compounds mixed to a 10-cm depth survived longer than compounds in experimental systems in which only a 3-cm depth was mixed. Not only was the longevity of contamination extended, but the concentration of tissue contamination of small clams (*Protothaca staminea*) was greater for the system mixed to a 10-cm depth.

The fate of polycyclic aromatic hydrocarbons taken up by marine biota is governed to a large extent by cytochrome P-450 enzyme systems. While significant research on these enzyme systems in nearshore and estuarine biota has been reported in the past several years, there have been very few investigations of these important xenobiotic activation and detoxification systems in deep-sea organisms. Stegeman reports on microsomal electron transfer component cytochromes in hepatic microsomes from several species of deep-sea fishes from depths of 1400 to 3200 m in the North Atlantic. Cytochrome P-450 contents were within the range observed for shallow-water fish species. The evidence suggested that hepatic cytochrome P-450 may have been induced in a few species by xenobiotics.

This brings us to the question of the extent of petroleum contamination of the North Atlantic waters. Van Vleet et al. took the significant step of combining pelagic tar measurements with physical oceanographic data and estimating an annual flux of 7000 t of pelagic tar from the Gulf of Mexico to the North Atlantic Ocean through the Straits of Florida. One half of this flux seems to originate in the Gulf, while the other half apparently enters the Gulf via the Loop Current from the Caribbean. Chemical analyses and time series sampling have suggested that large amounts of oil from the world's largest accidental oil spill — IXTOC I, off the coast of Mexico — have not crossed the Gulf to Florida's coastal waters. The depth distribution of pelagic tar based on net tows suggested that most of the tar is in the upper 50 cm of the water column. Concentrations ranged from 0 to 45.3 mg/m^2.

In contrast, Levy measured 0–85 $\mu g/m^2$ of pelagic tar in the more remote and more pristine area of the North Atlantic off Canada in the Grand Banks area. Levy also established that concentrations of methane, ethane, propane, and petroleum hydrocarbons in the water column and sediments were very low but may still be caused in part by initial exploratory drilling activities in the region.

The papers concerned with the biogeochemistry of fossil fuel compounds in the marine environment represent a cross-section of the state-of-the-art research on this subject. They range from the problems of longer term, larger scale measurement efforts for suspended tar to the details of metabolism of individual polynuclear aromatic compounds. The discussions at the conference indicated that substantial research is in progress in the important and exciting areas of photochemical and biological transformation of fossil fuel compounds, physical–chemical considerations such as partitioning between particles and solution, and the influence of macromolecular organic matter in aquatic systems on fossil fuel compounds in waters. The important problem of quantification of chronic inputs from urban areas has been researched and the path to gaining better national and global estimates for these inputs has been carefully set forth. Major contributions to understanding biogeochemical cycles of fossil fuel compounds in coastal and estuarine areas have been made by use of mesocosm studies.

Continued application of combinations of field studies, mesocosm studies, and smaller scale laboratory efforts seems to be the appropriate manner to achieve further understanding of the biogeochemistry of fossil fuel compounds in the marine environment. No single approach of these three is clearly more important to progress at this time.

SESSION II

Heavy Metals

CO-CHAIRMEN

HERBERT WINDOM

Skidaway Institute of Oceanography, Savannah, GA 31406, USA

AND JACK F. UTHE

Department of Fisheries and Oceans, Resource Branch, Halifax, N.S. B3J 2S7

Use and Relevance of Analytical Intercomparison Exercises in Monitoring the Marine Environment[1]

A. V. HOLDEN, G. TOPPING,[2] AND J. F. UTHE[3]

Freshwater Fisheries Laboratory, Department of Agriculture and Fisheries for Scotland, Pitlochry PH16 5LB, Scotland

HOLDEN, A. V., G. TOPPING, AND J. F. UTHE. 1983. Use and relevance of analytical intercomparison exercises in monitoring the marine environment. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 100–110.

The results of several intercomparison exercises for heavy metals and organochlorine residues in marine samples are reviewed. We conclude that, with few exceptions, the levels of agreement between the participating analysts are not good enough to allow them all to take part in multilaboratory monitoring programs, particularly with respect to monitoring residues in fish to determine whether they comply with standards set for human consumption or for comparing levels of contamination in different areas. Reproducibility of analysis is generally better at the higher concentrations and may be sufficient to measure a decrease in contamination following the removal of a highly polluting discharge. However, at the lower concentrations existing in cleaner environments many techniques that analysts currently use may be unable to achieve a degree of precision (or accuracy) sufficient to measure long-term trends in contamination. Analyses carried out by individual laboratories for the purpose of measuring trends in contamination levels must include regular intralaboratory checks to ensure a constant level of performance throughout the period of study.

HOLDEN, A. V., G. TOPPING, AND J. F. UTHE. 1983. Use and relevance of analytical intercomparison exercises in monitoring the marine environment. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 100–110.

Nous passons en revue les résultats de plusieurs travaux dans lesquels sont comparés les métaux lourds et les résidus organochlorés dans des échantillons marins. Notre conclusion est que, sauf dans quelques cas, il n'y a pas suffisamment d'accord entre les divers analystes pourqu'il leur soit possible de participer à des programmes de surveillance impliquant plusieurs laboratoires, en particulier en ce qui à trait aux résidus dans les poissons en vue de déterminer s'ils sont conformes aux normes pour consommation humaine ou de comparer les niveaux de contamination dans différentes régions. La reproductibilité de l'analyse est généralement meilleure aux concentrations élevées, et il se peut qu'elle suffise pour mesurer une diminution de contamination après disparition d'un effluent hautement polluant. Cependant, aux concentrations plus faibles que l'on rencontre dans des milieux moins contaminés, il est possible que plusieurs des méthodes présentement utilisées ne soient pas assez précises pour mesurer les tendances à long terme d'une contamination. Il faudra des vérifications intralaboratoire régulières des analyses menées par des laboratoires individuels visant à mesurer les tendances des niveaux de contamination afin d'assurer une performance uniforme tout au long de la période d'étude.

Received March 19, 1982
Accepted September 27, 1982

Reçu le 19 mars 1982
Accepté le 27 septembre 1982

A number of comparison exercises have been undertaken over the past few years among laboratories engaged in the analysis of various types of samples from the marine environment for heavy metals and organochlorine residues (Holden 1975; Holden and Topping 1981; IAEA 1978, 1980; Topping 1982; Topping and Holden 1978; Uthe and Musial 1980). In view of the generally poor levels of agreement found between most of the participating analysts, we believe that a review of the aims of the various analytical programs is appropriate and that consideration should be given to the possibilities for improvements in analytical expertise, which are necessary if these aims are to be achieved.

For several contaminants, the ranges of values reported for a single sample (intercomparison study) by the participants in these exercises have extended over more than an order of

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Marine Laboratory, Department of Agriculture and Fisheries for Scotland, Aberdeen AB9 8DB, Scotland.

[3]Present address: Department Fisheries and Oceans, Fisheries and Environmental Sciences, Halifax Laboratory, Halifax, N.S. B3J 2S7.

Printed in Canada (J6852)
Imprimé au Canada (J6852)

magnitude, and occasionally two orders. This variability was considerably greater than would be expected if experienced analysts used a single method (Burke 1979), but even in such a situation a coefficient of variation (relative standard deviation) of ±15% was not unusual and was often the lowest attainable. This implies a twofold range of reported concentrations for 19 out of 20 laboratories. Those not familiar with chemical analysis or similar types of measurement of physical properties are inclined to attribute to the sophisticated apparatus in the hands of a trained operator a degree of precision and accuracy which is quite unjustified. As Horwitz (1979) has pointed out clearly, all measurements are subject to variability, and there is high probability that a second measurement will differ from the first, unless the resolution of the instrument is too low. In analysis, variability is inevitable, but it can often be minimized.

Purposes of Analysis

There may be several reasons why an analyst is engaged in the determination of environmental residues on a regular basis, in a so-called monitoring program, but four examples will be sufficient to indicate the problems that can arise in the use of the data obtained. Firstly, consider that an area may be heavily contaminated and action may be taken, perhaps by legal imposition, to control or eliminate the offending discharge. It will be anticipated that the level of contamination will decrease, perhaps rapidly, but at least very significantly, and a fall in concentration of the contaminant by a factor of 10 or even 100 in certain components of the system will be expected. The analytical accuracy and precision needed to confirm this need not be high, and a rough determination of concentrations could be sufficient to demonstrate the effectiveness of the control measures.

Secondly, consider the monitoring of the fish and shellfish in a contaminated environment where their acceptability for human consumption must be determined. For many substances the maximum residue limits are at the parts per million level and relatively easy to detect, although recoveries may fall short of the total by 10−15% and precision may be ±15% or more in the determination of the amount extracted. For values close to the maximum residue limit, there is therefore bound to be some uncertainty whether the limit has been exceeded, and consignments may be rejected or accepted unjustifiably. Two analytical laboratories may differ considerably in their estimates of the level of contamination, and this can lead to international problems if the commodity is exported. The precision of a mean value can be improved by increasing the number of replicate analyses, but in practice this is costly and rarely acceptable. Horwitz et al. (1980) have suggested that at the parts per million (milligrams per kilogram) level of pesticide residues (and this could be equally valid for metals) the coefficient of variation is likely to be at least ±15%, whereas at the parts per thousand level it could be as low as ±4−5%.

For the third example, consider the determination of concentrations of substances at the so-called baseline levels in the environment. For organochlorines and some heavy metals this can mean parts per billion (micrograms per kilogram) or possibly even lower. Horwitz et al. (1980), in demonstrating that the interlaboratory coefficient of variation increased exponentially with decreasing concentration, suggested that at the micrograms per kilogram level it might be at least ±50%. Such low concentrations will in many instances stretch the ability of the technique used, and determinations close to the limit of detection will inevitably be imprecise. Yet at such low concentrations the analysts may be expected to produce data which are good enough for the calculation of trends in environmental contamination over periods of years! During such periods it must also be recognized that analysts, like methods or apparatus, will change; all these factors could have more impact on differences in concentration estimates than real changes in the environment.

The fourth example is perhaps the most important in the context of analytical performance. For some substances, such as cadmium, the maximum recommended limit for human consumption may be much closer to the limit of detection of the most commonly used methods than is the case for many contaminants, and thus, confidence in determining the environmental level with an acceptable degree of accuracy and precision will be low. In such instances a major improvement in the analytical technique is required so that the limit of detection can be brought well below the level of occurrence. This might involve a more sensitive method of detection or a preconcentration procedure which will enable higher concentrations to be presented to the measuring instrument.

Although not a subject for discussion in this paper, it should also be borne in mind that the sampling variability in the environment could be a major factor responsible for differences between samples in different years. Does the sample represent the same population in the same position, at the same time of year? Was it in the same physiological condition as the previous sample? Was it of the same age or age composition? Does it reflect today's contamination, or yesterday's or last week's, at the sampling site, or somewhere else? If these questions cannot be answered satisfactorily, the analyst could be wasting time and money in examining the sample.

Purpose of Intercomparison Exercises

It would not be realistic to expect all laboratories in an exercise to report identical values for specified residues in a sample, but it might be hoped that the interlaboratory variance of the data would be small so that the majority of analysts would report values within, for example, ±10% of the mean. Except when high concentrations of certain organochlorines have been spiked in a single matrix, or when high concentrations of certain metals have been present, this level of agreement has never been obtained in any of the published exercises (Holden 1975; Holden and Topping 1981; IAEA 1978, 1980; Topping 1982; Topping and Holden 1978; Uthe and Musial 1980).

These exercises have provided an opportunity for some analysts to test their techniques on samples of a type with which they may be unfamiliar and to compare their methods with those of others; however, not all analysts have accepted that they would find it advantageous to change or improve their technique. For some residues, usually at the lowest concentrations, agreement even within an order of magnitude has not been achieved. For some purposes, precision rather than

accuracy is important (e.g. for a laboratory engaged in trend analysis), but for most purposes a fairly high degree of accuracy is expected. Coordinated monitoring, if it is to have any value in enabling conclusions to be drawn regarding both trends and the comparison of different areas, demands both adequate precision and accuracy.

If intercalibration or intercomparison studies could demonstrate an acceptably high level of agreement among analysts, certain qualifications would still have to be recognized. This agreement would have been obtained when the analysts were fully aware of the nature of the test and that they were to be compared with others. In such circumstances, it is not unnatural that extra care may have been taken and that the apparatus and instruments were brought to the highest standard attainable with respect to cleanliness, adjustment, and the renewal of replaceable components. New standards are often prepared for the purpose; thus, the results may be somewhat better than those obtained in routine analyses, and the precision of the analysis in the exercise is possibly higher than for routine samples.

Regular testing by intercalibration or intercomparison is highly desirable to ensure that the analytical quality is maintained, although such testing can rarely be carried out "blind." If new apparatus is acquired, the analytical method modified, or the analyst replaced by another, intercalibration or intercomparison exercises become even more important. When their purpose is to assess whether data from routine sampling are mutually acceptable between countries, it is essential that the analyst responsible for the latter is also the analyst who processes the intercalibration or intercomparison sample.

Experience in Intercomparison Exercises

Analytical intercomparison exercises have been carried out within the framework of the International Council for the Exploration of the Sea (ICES) for several years, involving the determination of both heavy metal and organochlorine residues in organic matrices mostly of marine origin (Holden and Topping 1981; Topping 1982; Topping and Holden 1978; Uthe and Musial 1980). The authors, who have had the responsibility for preparing and distributing the samples and of assessing and reporting the results, now consider that the objectives of these exercises must be reexamined in the light of the experience gained.

During the past 8 yr the number of laboratories participating in the intercalibration exercises has increased. Several of them have examined all of the samples distributed for either metals or organochlorines, according to their particular interest. Some have been able to improve their analytical performance as a result of this experience, but in each exercise new laboratories have joined the participants and some have found difficulty in achieving an adequate level of precision or accuracy.

The extent of agreement between the analysts for the results reported for any metal or organochlorine residue was assessed by the analysis of variance and the calculation of coefficients of variation, usually after the exclusion of outliers according to a specified rule. Even the best data still yield coefficients of variation of 10–15% between analysts for certain organochlorine residues at concentrations two to three orders of magnitude higher than baseline levels, although for some metals, coefficients of variation as low as 10–15% have been achieved among the most experienced analysts at normal environmental levels.

On the other hand, the data for several metal and organochlorine residues at low concentrations gave coefficients of variations as high as 30–60% and sometimes even higher. In such cases, 19 out of 20 analysts will have reported values that are likely to cover at least an order of magnitude. For example, if the coefficient of variation for 20 analysts attempting to analyse a sample containing 0.5 mg Hg/kg is ±40%, it is probable that the range of values reported by them will be at least 0.10–0.90 mg/kg (±2 SD). This is clearly unsatisfactory. Even with a coefficient of variation of ±20%, the range 0.30–0.70 mg/kg is excessively large if the maximum acceptable concentration is 0.50 mg/kg.

The extent of agreement among the analysts participating in international intercomparison exercises in general has never been particularly high. Table 1 shows the coefficients of variation calculated for several metal concentrations reported in the samples provided for five ICES metal intercomparison exercises and other similar studies, and Table 2 gives the corresponding values for a number of organochlorines in the first four ICES exercises and some other studies involving this type of analysis. Extreme outliers (differing by more than 3 SD from the mean) were excluded from the ICES organochlorine data, although the elimination of more than 15% of the values has usually been avoided. Where a large proportion of values were reported as less than the limit of detection, their rejection may bias the calculation unduly. However, in some of the metal series the limiting values differed widely and were scattered throughout the range of reported values.

Assuming that the accuracy and precision of routine analyses of biological samples such as fish and shellfish are no better than for the intercomparison samples, and possibly worse, the results of coordinated monitoring involving the same or similar laboratories in different countries cannot give a true indication of the relative levels of contamination in fish and shellfish samples of similar type from these countries. The best that can be achieved is a distinction between areas of high and low contamination. Moreover, as the accuracy and precision decrease with decreasing residue concentrations, and most intercomparison samples for organochlorines have usually contained higher concentrations than those found in normal samples (to ensure that the data submitted are likely to be amenable to statistical analysis), it is probable that the accuracy and precision of routine analyses are actually *lower* than for the intercomparison samples.

Statistical Considerations

Given a homogeneous sample for distribution, unaffected by storage or biological degradation, the two sources of variance in analysis are those within each laboratory and those between laboratories, both essentially due to the analysts themselves. The within-laboratory variation is commonly one-half to two-thirds of the between-laboratory variation, in the experience of Horwitz et al. (1980). In many studies, the participants have used one recommended method (the "collaborative" study) (Burke 1979). In the ICES-sponsored

TABLE 1. Results of international laboratory intercomparison exercise for heavy metals.

Element	Reference material	No. of participants	Range of values (mg/kg)	Mean (mg/kg)	Coefficient of variation	Reference[b]
Copper	Fish flesh	64	0.5–17.6	4.5	53	1
	Fish flesh	20	2.7–5.7	3.8	18	2
	Fish flesh	36	0.4–4.0	1.8	39	3
	Sea plant	67	3.3–43	12.6	26	4
	Copepod	56	4.5–16.3	7.7	19	4
	NBS orchard leaves	10	9.9–13.0	11.6	8	5
	Plant material ("Bowen's" Kale)	88	—	4.8	15	6
Zinc	Fish flesh	74	4.0–204	33	26	1
	Fish flesh	21	28–53	38	16	2
	Fish flesh	36	13–37	23	18	3
	Sea plant	75	1.5–225	64	27	4
	Copepod	66	4.2–247	159	15	4
	NBS orchard leaves	11	18–29	24	14	5
	Plant material ("Bowen's" Kale)	77	—	32	15	6
Mercury	Fish flesh	29	0.93–1.80	1.36	17	7
	Fish flesh	29	0.03–0.21	0.10	60	7
	Fish flesh	52	0.18–3.5	0.49	29	1
	Fish flesh	16	0.74–1.36	0.85	7	2
	Fish flesh	33	0.05–0.37	0.21	33	3
	Fish flesh	34	0.01–0.25	0.06	50	3
	Sea plant	75	0.05–5.6	0.33	43	4
	Copepod	43	0.04–3.6	0.27	48	4
	NBS orchard leaves	11	0.10–0.20	0.15	25	5
	Plant material ("Bowen's" Kale)	9	—	0.15	5	6
	Blood[a]	18	0.2–9	2.6	81	8
	Urine[a]	29	4.9–63	13.0	82	8
Cadmium	Fish flesh	41	0.02–1.1	0.17	150	1
	Fish flesh	21	0.03–1.8	0.08	75	2
	Fish flesh	35	0.005–0.99	0.033	87	3
	Crab (brown meat)	52	0.53–1.11	0.80	17	9
	Sea plant	46	0.11–24	0.7	96	4
	Copepod	43	0.34–3.0	0.75	26	4
	NBS spinach	35	0.16–9.6	1.66	84	10
	NBS orchard leaves	35	0.01–2.26	0.26	145	10
	NBS tomato leaves	35	0.5–4.1	2.3	31	10
	NBS oyster tissue	35	0.4–12.0	3.7	50	10
	Blood	17	0.03–7.3	1.5	116	8
Lead	Fish flesh	33	0.1–5.1	0.8	71	1
	Fish flesh	21	0.16–4.0	1.1	83	2
	Fish flesh	32	0.02–7.5	0.21	71	3
	Fish meal	52	0.22–7.8	2.7	47	9
	Lobster hepatopancreas	32	0.11–3.2	0.75	71	9
	NBS spinach	35	0.4–7.5	1.6	97	10
	NBS orchard leaves	35	17.8–61.7	38.5	20	10
	NBS tomato leaves	35	0.5–13.0	4.8	52	10
	NBS oyster tissue	35	0.1–7.0	1.0	124	10
	Blood[a]	52	10.3–87	24.1	43	8
	Urine[a]	34	8.4–185	84	50	8

[a]Concentration units for blood and urine are micrograms per 100 mL and micrograms per litre, respectively.
[b]References: 1, IAEA (1980); 2, Topping and Holden (1978); 3, Holden and Topping (1981); 4, IAEA (1978); 5, IDOE (1972); 6, Bowen (1967); 7, Uthe et al. (1971); 8, Berlin et al. (1974); 9, Topping (1982); 10, Knowles and Burrell (1981).

studies and most similar exercises, analysts were mainly requested to employ their own methods of analysis for metals and organochlorines.

In monitoring fish and shellfish for human consumption,

TABLE 2. Comparison of results of international laboratory intercalibration exercises for organochlorines.

Residue	Reference material	No. of participants	Mean (μg/kg)	Range (μg/kg)	Coefficient of variation	Reference[a]
HCB	Corn oil (spike only)	7	46	14–70	41	2
	Fish oil	22	67	34–116	33	3
	Fish oil	15	35.5	13–70	41	4
	Butter fat	78	9.9	3–21	79	5
	Spiked butterfat	160	242	36–420	33	5
	Spiked butterfat	164	47	20–100	36	5
α-HCH	Fish oil (spike only)	14	709	—	15	1
	Fish oil	4	80	10–130	70	2
	Fish oil (spike only)	8	750	630–890	14	2
	Corn oil (spike only)	8	52	42–85	28	2
	Fish oil	20	11	1–25	71	3
	Fish oil	5	18	<5–50	89	
	Spiked butterfat	177	115	7–745	90	5
	Oyster tissue	17	9	0.9–20	43	6
	Sea plant tissue	19	16	0.3–23	38	6
pp'-DDE	Chicken egg	16	127	80–230	32	1
	Fish oil (spike only)	15	4476	—	13	1
	Fish oil	9	450	340–780	30	2
	Fish oil (spike only)	9	5260	4100–6300	20	2
	Corn oil (spike only)	9	101	83–128	14	2
	Fish oil	27	80	32–139	38	3
	Fish oil	17	221	21–343	26	4
	Butterfat	94	22	2–91	61	5
	Butterfat	190	196	20–410	28	5
	Spiked butterfat	172	784	320–1220	24	5
	Oyster tissue	23	88	30–200	48	6
	Sea plant tissue	17	7	2–12	42	6
TDE	Chicken egg	12	46	20–100	51	1
	Fish oil (spike only)	16	2909	—	21	1
	Fish oil	9	290	190–480	29	2
	Fish oil (spike only)	9	3040	2420–4000	18	2
	Corn oil (spike only)	8	217	200–257	10	2
	Fish oil	21	88	36–180	38	3
	Fish oil	14	80	12–320	101	4
	Butterfat	45	14	2–27	108	5
	Spiked butterfat	184	421	50–1980	49	5
	Oyster tissue	17	36	9–51	36	6
	Sea plant tissue	13	7	2–17	59	6
pp'-DDT	Chicken egg	16	445	140–620	31	1
	Fish oil (spike only)	15	4251	—	16	1
	Fish oil	9	430	330–610	21	2
	Fish oil (spike only)	9	4990	4500–5900	11	2
	Corn oil (spike only)	10	196	175–220	7	2
	Fish oil	25	113	30–220	44	3
	Fish oil	12	149	25–480	91	4
	Butterfat	67	24	4–80	182	5
	Spiked butterfat	186	550	30–920	21	5
	Oyster tissue	22	76	2–161	59	6
	Sea plant tissue	22	20	0.5–44	65	6
Dieldrin	Chicken egg	16	162	80–240	28	1
	Fish oil (spike only)	15	1257	—	17	1
	Fish oil	7	115	70–210	55	2
	Fish oil (spike only)	8	1440	1300–1600	7	2
	Corn oil (spike only)	9	93	53–120	24	2
	Fish oil	17	79	12–129	37	3
	Fish oil	10	58	14–140	63	4
	Butterfat	82	27	6–90	39	5
	Butterfat	98	26	5–170	125	5
	Spiked butterfat	159	107	20–1100	98	5
	Spiked butterfat	177	117	30–230	116	5

TABLE 2. (*Continued.*)

Residue	Reference material	No. of participants	Mean (μg/kg)	Range (μg/kg)	Coefficient of variation	Reference[a]
	Oyster tissue	13	12	0.5–27	67	6
	Sea plant tissue	11	10	6–17	40	6
PCB	Fish oil (spike only)	14	9230	—	12	1
	Fish oil	9	1890	1000–3900	48	2
	Fish oil (spike only)	9	9960	8300–11800	11	2
	Corn oil (spike only)	10	1059	944–1190	9	2
	Fish oil	15	451	172–900	45	3
	Fish oil	23	1070	48–1810	31	4
	Spiked fish oil	23	1930	700–2550	21	4
	Oyster tissue	14	310	50–561	55	6
	Sea plant tissue	14	190	8–470	63	6

[a]References: 1, Holden (1975); 2, Topping and Holden (1978); 3, Holden and Topping (1981); 4, Uthe and Musial (1980); 5, Snelson (1976); 6, IAEA (1976).

values of the maximum permitted concentrations (or maximum residue limits, MRL) are used as the basis of acceptability. The concentration of a particular contaminant, as determined by the analyst, will be qualified by estimates of accuracy (if available) and precision. For many contaminants, it is possible that the 95% confidence limits for a single analytical determination will be no better than ±40% (coefficient of variation = ±20%); thus, to have reasonable confidence that a MRL of 0.5 mg/kg, for example, will not be exceeded, values above 0.36 mg/kg would not be acceptable. (Those who analyse for mercury in fish will appreciate that a working limit of 0.36 mg/kg could result in the rejection of considerably more samples than one of 0.5 mg/kg.)

The alternative is to accept a 20% excess over the nominal limit of 0.5 mg/kg. In such circumstances, analytical data up to 0.5 mg/kg are accepted in the knowledge that a proportion will be likely to exceed 0.6 mg/kg and that 1 in 40 will be likely to exceed 0.7 mg/kg (1 in 40 will also be likely to fall below 0.3 mg/kg, i.e. 5% are outside the ±40% limits). This is a practical method of dealing with the problem, but would it be legal?

Considering now the question of measuring concentrations below the MRL, is there any justification for attempting to determine levels below 10% (or even 20%) of this value? It could be helpful to analysts to instruct them to restrict their limit of detection to 10% of the MRL for the purpose of food monitoring, rather than to expect them to operate their analytical technique at its maximum level of sensitivity. However, when measurements are required at or near the limit of detection, further consideration must be given to the statistical accuracy of the measurements.

Cheeseman and Wilson (1978), in discussing the statistics of detecting small concentrations, have shown that if the limit of detection (for a single determination) is defined as the level at which there is a desirably small probability (95% level) that this will be less than the criterion of detection, the limit is $4.60\sigma_w$, where σ_w is the within-laboratory standard deviation for measurements at such small concentrations. (The criterion of detection is that level at which one can have 95% confidence that the value is greater than the blank value.) In a recent ICES exercise for cadmium analysis in fish flour (Topping 1982), 52 participants reported their mean values and within-laboratory coefficients of variation. Over half achieved coefficient of variation values no greater than 5% at a mean concentration of 0.8 mg Cd/kg. Thus, the standard deviation at this level was 0.04 mg/kg or better, and the limit of detection based on this value would be 0.19 mg/kg. The provisional tolerable weekly intake of 400–500 μg Cd/adult (FAO/WHO 1972) can be reached by the consumption of 10 kg of food averaging 0.04 mg/kg wet weight, a value well below the limit of detection for which analysts could have any confidence.

However, although the coefficient of variation increases as the level of determination decreases, the analytical procedures adopted may enable the analyst to present concentrations to his apparatus that are not as wide ranging as in the original samples, and although the extraction or digestion stages may be the sources of some component of the error, the variance could be mainly due to the measurement stage. In an earlier exercise for cadmium (Holden and Topping 1981), the reported values for both the concentrations and coefficients of variation varied widely, but many laboratories achieved a coefficient of variation of ±15% or less at a concentration of the order of 0.03 mg/kg. The limit of detection from these figures would be 0.02 mg/kg, which is an improvement on the value calculated earlier in this paper but is still high for an adequate calculation of the average daily intake for a human population.

For mercury, the situation is more satisfactory. In two exercises for this element (Holden and Topping 1981), half of the laboratories achieved individual coefficients of variation of 8% or less at about 0.2 mg/kg, and at 0.05 mg/kg the coefficient of variation was 12% or less for half of the participants. These values suggest limits of detection of 0.07 and 0.03 mg/kg, respectively, both well below the maximum acceptable mercury concentration of 0.50 mg/kg in fish.

In the case of organochlorine analysis, determinations of the within-laboratory coefficients of variation have been reported only in one of the ICES exercises. Uthe and Musial (1980) reported within-laboratory coefficients of variation of 10 and 3% for unspiked and spiked herring oils (1 and 2 μg polychlorinated biphenyl (PCB)/g oil), and determined for

their intercomparison study that interlaboratory variation was the major source of the overall variance characterizing the submitted results. Values also have been recorded in the literature as the result of collaborative studies on pesticides in food or various types. Many of these studies used fortified (spiked) samples in which the background matrix was probably insignificant or at least likely to give the minimum of interference in the determination of the spike. The within-laboratory coefficients of variation reported by Horwitz et al. (1980) were of the order of 10−15% for individual pesticides. These authors considered that the within-laboratory repeatability to be expected is approximately 10% at the milligram per kilogram level and 20−25% at the microgram per kilogram level. Such values are obtained under particular conditions when the analyst is taking perhaps greater care than usual to obtain results, and Burke (1979) suggests that the overall estimate of inevitable variability from all sources, including sampling, for pesticides at food tolerance levels is about 25% for single analyses.

Most interlaboratory studies of organochlorine analyses have reported only the overall interlaboratory coefficients of variation. The overall impression gained from these exercises (Table 2) is that the interlaboratory coefficients of variation for concentrations of the order of 1−10 mg/kg lie in the range 10−20%, at 0.1−1 mg/kg in the range 20−50%, and at the lowest concentrations of 0.01−0.1 mg/kg in the range 30−70%. Less than half of this variation is likely to be due to within-laboratory repeatability.

However, no exercises using typical baseline environmental concentrations of 0.001−0.01 mg/kg have been undertaken, but it seems probable that the interlaboratory variation could be at least 50−100% in this range, with perhaps 20−40% for within-laboratory repeatability. Add to this the inevitable sampling variability in an environmental program extending over a long period, and it is very doubtful whether the overall variation would enable small trends in baseline contamination to be detected, even when investigated by a single laboratory. A multilaboratory program would seem to have little chance of success.

Two factors might be considered in any attempts to improve the situation. Firstly, several replicate analyses on each sample would improve the precision of the mean, although this might be costly. Secondly, analysts could be encouraged or even compelled (as a condition of participation) to improve their techniques, perhaps by specifying the need for certain procedures at various stages of the analysis. Suggested improvements (or constraints) for heavy metal and organochlorine analytical techniques are given below.

One final consideration concerns the extent of participation in interlaboratory studies. If a selection of "good" laboratories is to be made subsequently, all can participate, but Burke (1979) considers that "if the purpose is to assess the quality of data coming from laboratories doing a certain type of (pesticide) residue analysis, it is usually desirable to include only those laboratories that are in fact actively engaged in that work." In consequence, marginal laboratories not experienced in the work, or not regularly engaged in it, should be excluded.

Sources of Variance

Among the possible sources of variance in the results submitted from an intercomparison exercise are (a) lack of homogeneity in the sample supplied, (b) deterioration of sample with time, (c) errors in subsampling of sample for analysis, (d) inadequate extraction of residue from the subsample portion, (e) errors in preparation of extract for analysis, (f) errors in subsampling of extract, (g) variance in technique used for residue determination, (h) inaccurate reference standards, (i) errors due to background interference, (j) instability of apparatus used for quantification, (k) errors in identification of residues, (l) errors in calculation of residue concentrations in original sample, and (m) unsatisfactory choice of preparative or analytical technique.

In the ICES exercises, great care has been taken to ensure that the samples prepared for distribution were homogeneous. Fish flour samples have been ground and blended for long periods, the finer powder being less likely to cause variations between small portions than fish meal samples. The oils used for organochlorine analysis have likewise been mixed thoroughly for long periods and have themselves mainly been taken from larger batches of commercial oils. No evidence of sample deterioration with time after distribution has been found from the results reported, either for heavy metals or organochlorines. To test for homogeneity, not less than 10 replicate analyses of the homogenate are desirable, and the variation should be no larger than for a standard reference material of similar type, if this is available.

The true residue composition of a natural sample cannot be known, and the results of analyses by a number of laboratories, perhaps using different techniques, can give only a consensus value. The addition of known concentrations of contaminants to the matrix (spiking), if carried out with sufficient accuracy, enables the estimates of this addition to be compared with a true value. However, it is often likely that the spike material is in a different chemical form from that in the matrix, particularly in the case of heavy metals or PCB added to tissue samples. It is then considered that the determination of the spike addition is not a realistic test of the ability of the analyst to determine the same residues in the matrix. While this is probably true, if the results of the intercalibration of the spike concentration are poor, those for the matrix are likely to be even worse. A high level of agreement obtained on the spike concentration would at least be encouraging.

The satisfactory preparation of a spiked intercalibration sample is impossible unless thorough mixing can be achieved. With liquids such as water or oil the mixing is usually successful if carried out thoroughly, but the addition of a spike solution to a powder such as fish flour or sediment and subsequent blending can be more difficult. The most successful procedure for liquids is to spike a small volume, mix this with a larger volume, and finally mix into the entire sample. The same methods can be used for solids, but the final result is likely to consist of a small percentage of coated particles in a largely uncontaminated matrix. Unless the particles are very small and blend very thoroughly, small portions of such a mixture are likely to be insufficiently homogeneous and the variation between portions could be unacceptably high.

To ensure that the statistical analysis of the data obtained for spike concentrations is not unduly influenced by the levels in the matrix, the latter must either be essentially free of residues (a virtual impossibility for natural materials in the marine environment) or the spike concentrations must be much higher than those in the matrix. Unfortunately, while the latter improves the quality of the estimates of the spike, it may draw the criticism that the concentrations are abnormally high and not a realistic test of the ability of the analyst to determine commonly occurring environmental levels.

Of the sources of error listed earlier, some will result in only minor variations and can be eliminated by more careful attention. Errors of calculation, or mistakes in recording volumes or dilution factors, could result in major variations among the results reported, and in a few instances analysts have notified the authors of these errors subsequently. Others may have been missed entirely. Methods of digestion (for heavy metals) or extraction (for organochlorines) are probably responsible for a certain amount of the variance observed among analysts.

The use of incorrect reference standards could be a major source of error. Topping and Holden (1978) reported that in an earlier exercise for mercury analysis some individual laboratory standards may have been faulty due to insufficient acidity, and this was drawn to the attention of the respective laboratories. Some working standards for copper, zinc, lead, and cadmium used by the laboratories were also shown to be a major source of error, and in some subsequent exercises a common stock standard was supplied with instructions for dilution. It is now more usual to ensure that participants acquire or make up their own reliable stock standards and produce working standards according to an accepted code of practice.

The major sources of variation for organochlorine analyses lie in the wide range of cleanup and separation techniques previous to gas–liquid chromatography (GLC) available, in confusing peak identity, or in the interference between residues if column resolution is inadequate. (The identities of heavy metals are rarely in doubt, although matrix interference is likely to be more significant in their determination.) Holden and Topping (1981) reported an apparent difference in the determination of PCBs resulting from the use of sulphuric acid in sample cleanup as compared with absorbent columns. Uthe and Musial (1980) examined the influence of individual laboratory standards for PCBs, as compared with a common standard supplied to all participants, and also compared data from a common method of calculation of PCB concentration with results from individual laboratory methods. However, neither the mean values nor the coefficients of variation in these four groups (common standard or method, own standard or method) were significantly different. Investigation of submitted results indicated that the two common absorbent columns used (alumina or Florisil) gave somewhat different results for PCB levels.

As the variance of the interlaboratory data includes a component due to the within-laboratory variance (which itself will vary among the laboratories), it is desirable that the variance within each laboratory should be as small as possible. Attention to the causes of variance listed above should ensure this, but all intercomparison exercises should include provision for the estimation of precision of the analyses reported by each participant. Determinations should be made on at least six separate portions of the sample, each taken through the entire analytical procedure. This has been undertaken in some of the heavy metal exercises but so far the cost of organochlorine analyses has usually prevented the same being undertaken for these residues.

With both atomic absorption spectrophotometry for metals and gas chromatography for organochlorines, recorders may be used to measure response, but unless carefully maintained these can be subject to major errors both from noise when the signal response is small and from nonlinearity of the signal–concentration curve. Electron-capture detection systems are also subject to nonlinear response, although this is generally recognized. When automatic integrators are used, major errors can result if their signal recognition systems are inadequate. In all interlaboratory exercises, it is essential that those assessing the results are supplied with details of the individual analytical techniques *and* examples of the recorder traces if these are used for measurement purposes. Numerical results alone may appear satisfactory, but an examination of the associated recorder trace may indicate whether the identification or quantification is justified. The contrast between the quality of chromatograms from packed and capillary columns, for example, can be very marked.

Suggestions for Improvement of Intercomparison Exercises

On an international scale it has not been possible for all analysts to use the same method. National organizations may enforce the use of their own selected methods, the individual analyst may have particular experience of a method of his choice, or perhaps the choice is dictated by the availability of certain chemicals or apparatus. International interlaboratory studies therefore involve a variety of methods and would be classified by Burke (1979) as "laboratory performance checks." The degree of variation between laboratories can thus be expected to exceed that attainable in collaborative studies, and the range of within-laboratory variances is also likely to be larger.

Most international intercomparison exercises so far carried out have given the analyst complete freedom of choice in selecting and employing his analytical techniques and have been designed to establish whether or not the degree of agreement achieved is adequate. As this agreement has not been close in most instances, it is now suggested that some restriction should be imposed in the choice of a suitable technique and that an indication should be given of the sensitivity required. It is inappropriate to designate particular makes of commercial apparatus, but the various stages of the analytical procedure could be stipulated and, where necessary, the degree of efficiency required at each stage. The tendency towards standardization should help to eliminate the variance due to the wide variety of techniques hitherto employed and enable analysts to report data that demonstrate a much higher degree of agreement than has been achieved so far in ICES or other exercises.

Analysts have had freedom of choice in the methods they employ in monitoring, also, and it may be advisable, if

coordinated monitoring is to continue, to ensure that analysts are capable of analyzing intercalibration samples and reporting data within prescribed limits before their routine analyses are to be accepted in international monitoring programs. The following paragraphs outline our suggestions for the specification of suitable analytical procedures for heavy metals and organochlorines, which should ensure some flexibility on the part of each analyst while eliminating possible major sources of variation between analysts.

Heavy Metals

The results of the ICES intercomparison exercises to date have shown that about half of the participants can produce comparable data (coefficient of variation approx. 10%) for copper, zinc, and mercury at concentrations which are typical of those encountered during monitoring programs for fish and shellfish and for cadmium at concentrations found in some shellfish. Unfortunately, however, the majority of participants do not produce comparable data for low levels of cadmium as found in fish muscle and for levels of lead (below 1 mg/kg) as encountered in fish muscle and in some shellfish. It is considered that the improvement in comparability for cadmium and lead at low levels in intercomparison exercises, and possibly monitoring programs, could be achieved by an improvement in the accuracy of the analytical procedures currently employed by participants.

There are four sources of systematic errors (bias) in analytical procedures for metals. These are (1) a biased blank correction, (2) a biased calibration, (3) the inability to determine all chemical forms of the element, and (4) the effect of other substances present in the sample, i.e. interferences.

1) In theory, a blank determination consists of the analysis of a special sample of the material of which normal samples are composed and which contains a negligible concentration of the determinand. In practice, in relation to trace metals in tissue, it is impossible to apply this principle, and most blanks consist of a reagent blank only. It is evident from an examination of the data submitted by participants in ICES exercises that the value of the reagent blank varies from laboratory to laboratory. The reduction of a blank value can be achieved by (a) ensuring that only high quality reagents and labware are used in analytical procedures and (b) that all labware is rigorously cleaned prior to use. Ideally, all analytical operations should be done in a specially constructed clean laboratory.

2) The adoption of a common procedure by all ICES participants for the preparation and use of working standards has eliminated one source of error in calibration procedures. Similarly, the adoption by a number of participants of "the method of standard additions" approach to analysis is thought to overcome the problems of interfering substances. The use of the method of standard additions is based on the assumption that the interfering substance alters the absorbance of the added metal to the same extent as it does that of the metal in the original sample. Some experts in the field of atomic absorption spectrophotometry consider that this may not always apply, particularly for low levels of metals injected into a graphite furnace. It is suggested therefore that participants should consider employing solvent extraction procedures (e.g. ammonium pyrrolidine dithiocarbamate – methyl isobutyl ketone or dithizone–$CHCl_3$) to separate the metals from the matrix prior to measurements in the graphite furnace. Some participants, who have consistently produced low values for cadmium and lead in tissues, have taken this separation even further by back-extracting the metals from the organic solvent into weak acid and injecting this solution into the furnace. In this way, one eliminates the need to prepare standards by solvent extraction, provided corrections are made for loss in the extraction stages. Although this procedure assumes all chemical forms of the metals in the digest are extracted with the same efficiency as the added chemical form, substantial improvement in interlaboratory precision should result from adoption of this procedure.

3) The metals may be present in several forms in the sample and each of these forms should be determined with equal efficiency. By adopting "dry" and/or "wet" ashing procedures analysts are endeavouring to convert all forms of the metal into the inorganic state. Some procedures are more rigorous than others in the destruction of the organic material. Some of the differences between data for cadmium and lead may well be associated with the different digestion procedures used by participants. If this is the case then analysts may well have to adopt a common digestion procedure to eliminate this source of error.

4) The incorporation of deuterium background correction in modern atomic absorption spectrophotometers has to a large extent eliminated the error due to absorption or scattering of light by solid particles in the light path. The absorption of light by the metal under examination may be influenced, however, by the sample matrix which can depress or enhance the absorption. One solution to this problem is the method of standard additions so that samples and standards are subjected to the same degree of interference. Alternatively, one can adopt the solvent extraction procedure discussed under 2. The latter approach is more preferable, from a practical viewpoint, since it avoids the necessity of multiple analyses of each sample.

Organochlorines

Agreement among analysts participating in ICES intercomparison exercises for organochlorines has only been good (coefficients of variation 10% or less) when determinations have been made of spike concentrations in a noninterfering matrix (tetrachlorodiphenylethane (TDE), dichlorodiphenyltrichloroethane (DDT), and PCB in corn oil) or when the spike concentrations were an order of magnitude higher than in an interfering matrix (dieldrin, DDT, and PCB in fish oil). For unspiked fish oils, the coefficients of variation for a number of residues have been mostly in the range 30–70%. A number of sources of potential error are possible, including impure solvents, inadequate cleanup to remove interfering lipids, lack of separation of PCB residues from other residues, poor resolution or sensitivity in GLC analysis, failure to concentrate extracts accurately and as much as possible, and variability in the volume of extract injected into the chromatograph.

The following suggestions are made for the improvement of techniques used for routine analysis, and for intercomparison exercises in particular: (1) high quality solvent; no significant

peaks interfering with organochlorine residues of interest after 100-fold concentration; (2) extraction for a minimum of 40 cycles in Soxhlet extractors (except for oil samples); (3) cleanup of a portion of the extract using absorbent columns; (4) pre-GLC separation of residues into at least two fractions, one containing all PCB; (5) concentration of fractions from 4 above to not less than 1 mL accurately measured; (6) use of internal standards to correct for errors at GLC injection stage; (7) use of packed GLC columns giving plate counts for *pp'*-DDE or dieldrin of not less than 3000 theoretical plates per column; (8) alternative to 7; use of capillary or WCOT (wall-coated open tubular) columns of at least 10 000 theoretical plates; (9) sensitivity of GLC detector response sufficient to give a response of five times recorder baseline width for 10 pg of *pp'*-DDE or dieldrin; (10) detector response to be within linear range with frequent calibration; (11) regular renewal of standard solutions and prevention of solvent evaporation.

General Conclusions

Future intercomparison exercises should be designed to assess the extent of improvements resulting from the implementation of certain recommended procedures. These procedures could be agreed by small groups of analysts experienced in heavy metal and organochlorine analysis selected from national or international groups as appropriate. It is recognized that spiking of a natural matrix may not result in the spiking being combined in the same manner as the identical substance in the matrix. However, it is suggested that unless good agreement among analysts can be achieved for spike additions it is unlikely that satisfactory agreement for lower concentrations in natural biological materials will be attainable. Spiked intercalibration samples may therefore be worthy of consideration, provided that they can be prepared in a sufficiently homogeneous form. Ideally, standard reference materials should be made available internationally.

Regular testing by intercalibration or intercomparison is highly desirable to ensure that the quality of analytical data is maintained among the group of analysts involved in monitoring programs. In these exercises provision should be made for inexperienced analysts to participate, since it is only by such an involvement that they can truly compare their analytical procedures and results with those of the more experienced analysts.

The authors consider that the future monitoring programs for a number of metal and organochlorine contaminants must consider the two options available if adequate agreement among all analysts cannot be achieved.

1) Data for surveys should only be accepted from those laboratories that continually demonstrate that they can achieve comparable results (interlaboratory coefficient of variation of 10% or less) from intercomparison samples at the appropriate environmental levels. Other laboratories could be asked to improve their analytical procedures or adopt proven techniques and would join the first group of laboratories after demonstrating satisfactory ability in a further intercalibration exercise.

2) As an alternative, acceptance of data from monitoring programs should be restricted to the higher concentrations of each contaminant, at levels for which satisfactory agreement among all analysts has been demonstrated. The first option is in our view the only one likely to be acceptable.

Finally, before analysts are asked to improve their analytical techniques for determination of low concentrations, it is essential that consideration be given by appropriate bodies to the concentration levels at which data of acceptable quality are required. It has been stated earlier that the coefficient of variation among analysts increases as the determinand concentration decreases. Analytical agreement may already be adequate for some contaminants which are of little toxicological significance to man, while it is quite inadequate at the present time for more hazardous substances. For instance, if the maximum acceptable daily intake of cadmium for man can be reached by the consumption of food averaging 0.04 mg Cd/kg wet wt, good agreement among analysts must be attainable at concentrations well below this. In practice, good agreement for cadmium was only achieved in the sixth ICES exercise at the equivalent of 0.2 mg Cd/kg wet wt. A similar problem arises with respect to lead.

The concentration levels for which good agreement is required may be established from the maximum acceptable daily intake with respect to human food consumption. Although there is also a need to protect the marine environment from the effects of pollution, so far no maximum acceptable levels for contaminant levels in fish tissue have been internationally agreed on for this purpose.

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The Distribution of Selected Trace Metals in United Kingdom Shelf Waters and the North Atlantic[1]

P. G. W. JONES AND D. F. JEFFERIES

MAFF, Directorate of Fisheries Research, Fisheries Laboratory, Lowestoft, Suffolk, NR33 OHT, U.K.

JONES, P. G. W., AND D. F. JEFFERIES. 1983. The distribution of selected trace metals in United Kingdom shelf waters and the North Atlantic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 111–123.

The distribution of dissolved and suspended particulate Cd, Cu, Mn, Ni, and Zn was surveyed in the water of the North Atlantic and adjacent European shelf seas. The exercise was conducted by the Lowestoft Fisheries Laboratory and was part of a broad program coordinated by the International Council for the Exploration of the Sea (ICES) Working Groups concerned with pollution baseline and monitoring studies. The distribution of dissolved metals was enriched in coastal waters up to an order of magnitude compared with the offshore shelf seas. Both anthropogenic and natural sources of metal were considered in relation to the elevated inshore values. The suspended particulate phase of trace metals present in coastal and shelf waters was often a significant proportion (between 5 and 70%) of the total metal present. Oceanic values of dissolved metal were comparable with concentrations measured in offshore shelf seas. Deep vertical profiles of trace metals resembled the distribution of nutrient salts, thus indicating biological mobilization. The validity of all data was discussed in relation to current sampling and analytical techniques. The degree of sampling and analytical sophistication employed must relate to the basic requirements of the exercise.

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Des relevés de la distribution de Cd, Cu, Mn, Ni et Zn dissous et particulaires ont été effectués en Atlantique nord et dans les mers épicontinentales avoisinantes d'Europe. Le travail a été mené par le laboratoire des pêches de Lowestoft dans le cadre d'un programme plus général coordonné par les groupes de travail du Conseil international pour l'exploration de la mer (CIEM) s'occupant d'études de niveaux de référence et de surveillance de pollution. Les eaux côtières sont plus riches en métaux dissous que les eaux du large des mers épicontinentales. On a tenu compte des sources tant anthropogènes que naturelles de ces métaux en rapport avec les niveaux élevés des eaux côtières. La phase particulaire en suspension de métaux en trace représente souvent une importante portion (entre 5 et 70 %) de la totalité des métaux présents. Les valeurs océaniques des métaux dissous sont comparables à celles du large des mers épicontinentales. Les profils verticaux profonds des métaux en trace ressemblent à la distribution des sels nutritifs, signe d'une mobilisation biologique. Nous examinons la validité de toutes les données dans le contexte des méthodes d'échantillonnage et d'analyse courantes. Le degré de raffinement de ces méthodes doit correspondre aux besoins fondamentaux du programme.

Received March 19, 1982
Accepted January 13, 1983

Reçu le 19 mars 1982
Accepté le 13 janvier 1983

MEASUREMENTS of the distribution of trace metals in the waters surrounding the British Isles were begun in our laboratory during 1967 as part of a program aimed at assessing the relationship between selected radionuclides in the marine environment and their stable element analogues. However, at that time, the scientific community was becoming increasingly aware of the role of trace metals from terrestrial discharges as potential pollutants in the marine environment. Thus, the Lowestoft study became progressively more oriented towards that aspect, and the results of the pilot Lowestoft investigation were published by Preston et al. (1972).

In 1971, the International Council for the Exploration of the Sea (ICES) established a working group for the International Study of the Pollution of the North Sea and its Effect on Living Resources and their Exploitation. The Lowestoft

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6853)
Imprimé au Canada (J6853)

Laboratory continued its program of measurements in the North Sea as a contribution to this project and, at the same time, surveys of other British coastal waters were continued. In 1975, the original ICES Working Group was expanded to have responsibility for pollution baseline and monitoring studies in the Oslo Commission and the International Commission for the Northwest Atlantic Fisheries (ICNAF) areas of the North Atlantic. The Lowestoft trace metal survey area was also extended to provide an input to the newly formed ICES group.

In 1974, the United Kingdom Government introduced the Control of Pollution Act (Great Britain Parliament 1974), which places a responsibility on local organizations concerned with water quality control to monitor and control the discharge of pollutants to freshwater, estuarine, and coastal marine waters. Although the part of the Act relevant to tidal waters has yet to be implemented, the data provided by these surveys will give useful baseline information in relation to the abovementioned statutory function. In addition, directives of the Council of the European Communities also require the regular monitoring of such potential pollutants in the tidal waters of member states.

The primary aim of these surveys was to assess whether or not the sea areas studied were being measurably enriched by trace metals from terrestrial sources. The difficulties encountered in both making such observations and interpreting the resultant data will be discussed later where appropriate. However, the chief merit of this exercise is considered to be the fact that a large number of observations have been made over a wide area by a single organization, and thus, data from different sea areas may be compared with a reasonable degree of confidence.

The main suite of four metals analyzed were Cd, Cu, Ni, and Zn. They were selected for their relative ease of determination and their potential as pollutants. Manganese was also measured but on a limited scale. Although fully recognized as a pollutant, Pb was not included in the present series owing to the considerable difficulty in obtaining contamination-free measurements of this element at the concentrations likely to be encountered (Patterson et al. 1976). The distribution of Hg was surveyed and published separately (Baker 1977).

Methods

Most surveys were made from the Ministry's research vessels, but some samples were collected during cruises of the Deutsches Hydrographisches Institut research vessel *Meteor*. Most surface samples were collected in a plastic bucket. All subsurface water and some surface samples were collected in Niskin-type bottles of varying capacity. Samples for filtration were processed immediately after collection by passing through acid-washed 0.22-μm Millipore membranes in an all-plastic pressure filtration unit. All water samples were then stored deep-frozen without acidification. To estimate particulate metals, the membrane used to filter the sample was generally retained for analysis and a subsample was filtered through a separate preweighed membrane to obtain the total weight of the suspended load.

Analysis of metals in both water samples and suspended particulate material was made by atomic absorption spectrophotometry. Organic extraction preconcentration techniques were used for the analysis of water samples. Mostly, an MIBK/APDC technique was employed based on that of Brewer et al. (1969). Some of the earlier analyses employed an extraction into chloroform, followed by conversion to a methanolic solution. Manganese was measured by this technique in addition to the four other metals. Measurements were made from a tantalum boat for Cd and direct aspiration into the flame for the remaining metals (Preston et al. 1972). Intercalibration of these techniques showed them to produce comparable results. After 1974, the measurement of all metals other than Zn was made by a flameless technique employing a graphite furnace. The high sensitivity for Zn permitted direct aspiration into the flame to be used throughout.

For the analysis of suspended particulate material, membranes were boiled with approximately 20 mL of HCl ($1\ mol \cdot L^{-1}$) for 10 min; the solution was then made up to volume and the metals were measured as above in the aqueous phase.

Throughout the investigation, minor modifications were made to the methods of both sample collection and analysis in the light of experience gained. Such changes generally reduced the possibility of sample contamination or increased the sensitivity of the analytical techniques.

In a situation where analyses have been performed over a relatively long time, it is difficult to make definitive statements regarding precision of measurement and limits of detection. For example, the acquisition of the graphite furnace improved the limits of detection for most metals and made the measurement of offshore Ni more realistic. In general, one assumes that the precision tended to improve over the period of the survey, and spot checks indicated such a trend. As an overall approximation, however, a value of ±5% would seem reasonable at the "median" level of concentration encountered, i.e. 0.05, 0.5, 5.0, 1.0, and 2.0 $\mu g \cdot L^{-1}$ for Cd, Cu, Mn, Ni, and Zn, respectively. Limits of detection after the acquisition of the furnace were approximately 0.01 $\mu g \cdot L^{-1}$ for Cd, Cu, and Ni and 0.1 $\mu g \cdot L^{-1}$ for Mn and Zn. Sampling precision was, at the time, difficult to quantify separately from analytical precision.

Metal values indicative of gross sample contamination were omitted before analysis of the data. In most instances these were the occasional relatively high values which appeared in offshore water samples and which were not supported by any other features which would substantiate their authenticity. However, some of the earlier values (notably Cd, but to a lesser extent Ni and Zn) were higher than observations recorded during later surveys. In the light of experience gained from intercalibration exercises, etc., these early values are considered to have suffered from sample contamination and are not included in the report.

Results and Discussion

The distribution of metals will be considered under the following geographical groups (Fig. 1): (i) United Kingdom shelf waters comprising the North Sea, English Channel, and Irish Sea; (ii) continental shelf waters to the west of Scotland and Ireland plus the Celtic Sea and western approaches to the

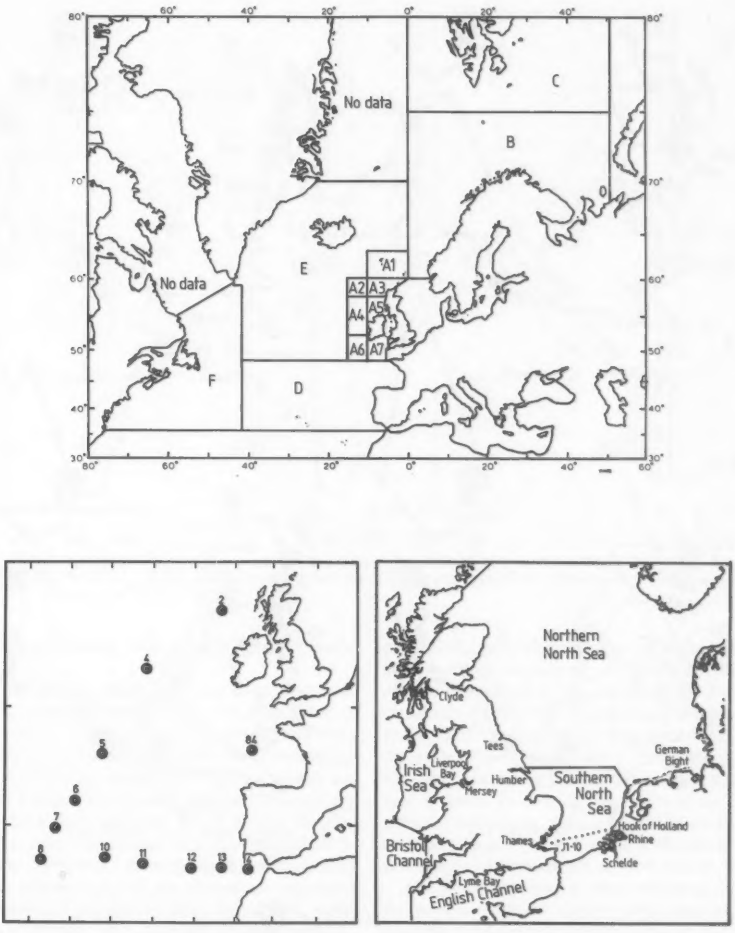

FIG. 1. Survey area for the North Altantic, vertical profiles, and United Kingdom shelf.

English Channel; (iii) the North Atlantic.

Only surface values are quoted for regions i and ii. Subsurface observations were also made at several stations but no consistent differences in the dissolved metal content of the water column were apparent, apart from some coastal locations near estuaries where high values at the surface were associated with freshwater discharges.

(i) United Kingdom Continental Shelf Waters

All samples were filtered prior to analysis. Early problems with metal contamination of the membranes prevented a reliable assessment of the suspended trace metal load on many of the surveys. This problem was eventually overcome by careful acid washing of the membranes, and data are presented on suspended particulate metal loads from some of the later surveys.

Distribution of dissolved trace metals — The mean distribution over all surveys of the North Sea, Irish Sea, and English Channel is depicted in Fig. 2. The number of observations and the area surveyed for Mn is less than for the remaining metals. The southern North Sea was surveyed by a fixed grid of stations and it was thus relatively simple to derive mean values for each location and then to contour concentration gradients. The position of contours for the remaining areas was assessed from visual comparisons of individual surveys. A broken contour indicates some degree of difficulty in locating a mean position owing to variability between cruises. A large part of the data relating to the

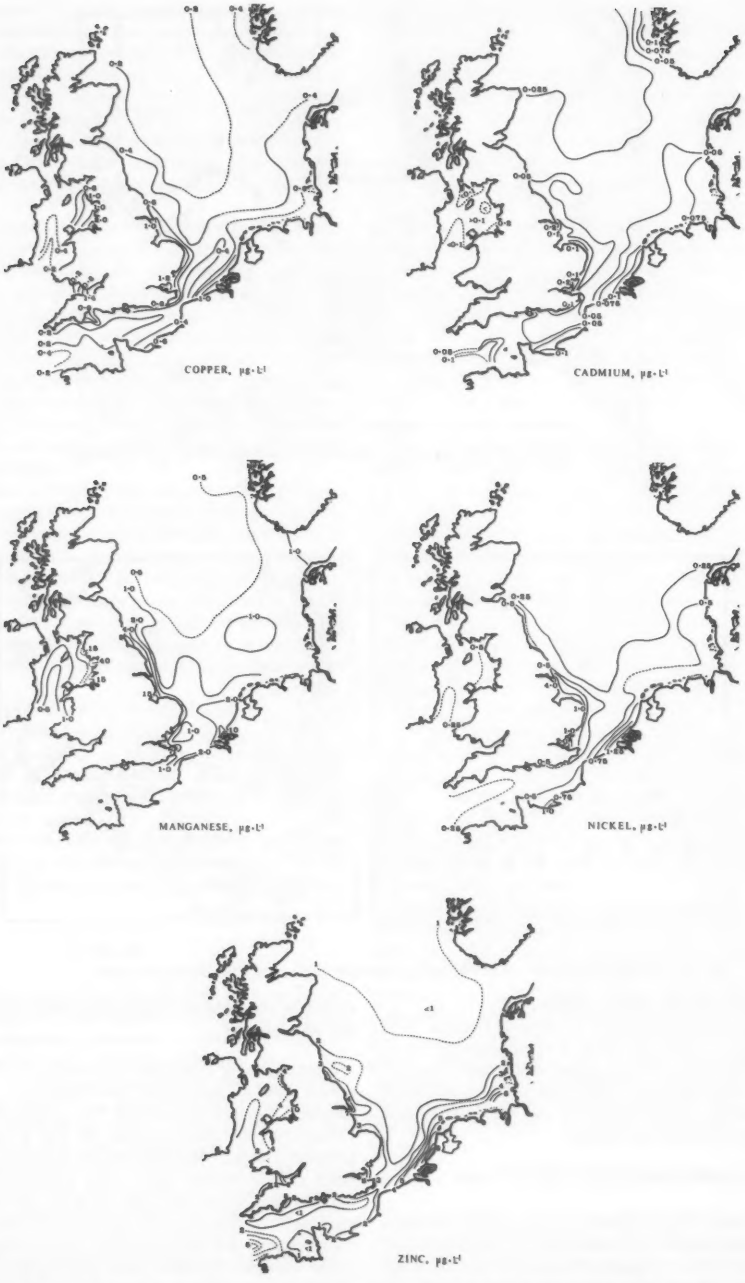

FIG. 2. Distribution of dissolved Cu, Cd, Mn, Ni, and Zn in the surface waters around the British Isles.

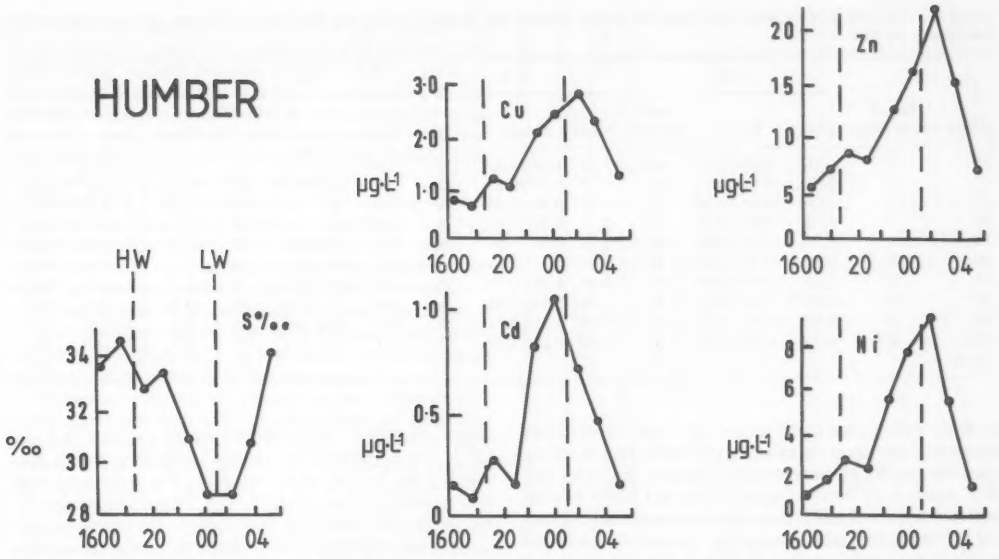

FIG. 3. Salinity and dissolved Cu, Cd, Zn, and Ni in the surface water during a tidal cycle at a station near the entrance to the River Humber during *Corella* cruise 5/73 (March 19–20, 1973).

English Channel was obtained from a single cruise (*Corella* 12/74).

The highest values of all metals generally occur in coastal waters, particularly near the major river discharges. Further offshore, notably in the northern North Sea, there are extensive areas of relatively low metal concentration. This configuration inversely reflects the mean distribution of salinity for the area (Lee and Ramster 1981) where the coastal waters are associated with the lowest salinities. We infer that the elevated coastal metal values are associated with terrestrial freshwater discharges. Moreover, measurements made within United Kingdom estuaries during the present investigation (results to be published elsewhere) have shown that metal levels continued to increase against salinity gradient profiles. Some observations made over 12.5-h tidal cycles near the entrance to the Humber Estuary (Fig. 3) clearly demonstrate the inverse relationship between salinity and trace metals.

The basic inference from these results is that industrialization and urbanization must play a large part in the observed coastal water metal enrichment from terrestrial sources. The fact that elevated metal levels are associated with, for example, the Thames Estuary and the Rhine/Schelde complex would seem to substantiate this hypothesis. However, it is interesting to note that the distribution of Cu and Zn (Fig. 2) in the English Channel indicates an intrusion of elevated values into Lyme Bay. Natural ores leach metals into several river systems of southwest England (Bryan et al. 1980). Although the major influence is farther to the west of the present observation, a natural source of metal must be a distinct possibility.

The configuration of contours for the Irish Sea proved particularly difficult to prepare owing to the degree of variation between one survey and another. However, this situation would seem to be related to the fact that the water circulation of this area is complex and subject to much variability (Jefferies et al. 1982; Ramster 1973). The main anomaly in the offshore zone is the tongue of elevated values of Cd, Cu, and Zn entering the western English Channel. This feature is based on one set of observations, but it has been included because it related to several observations across a relatively large area. If it is not a sampling artifact its cause and degree of permanence are not known.

The greatest number of observations at fixed points during the present series of surveys have been made on a section across the southern North Sea between the Thames Estuary and the Hook of Holland and known as the J line (Fig. 1). The data were used to assess the variability of Cd, Cu, Ni, and Zn recorded at each station (Table 1). The mean values for each metal confirm the configuration depicted in the contoured charts, with the highest levels occurring in coastal waters. The range and consequently the coefficients of variation, however, were relatively large for all metals at most stations. The mean of individual coefficients of variation for each metal ranged between 38 and 56%. Little was apparent in the way of clearly defined trends in this variability, except that Cd values showed the greatest percentage variability at the Thames Estuary end of the section whereas the reverse situation held for Cu. Several causes for such variability may be considered. Sampling at the coastal stations was not timed to coincide with any particular state of the tide. Thus, the metal levels would fluctuate according to the proportion of the freshwater component present at the time of sampling.

TABLE 1. Analysis of trace metal data from the section between the Thames Estuary and the Hook of Holland. All concentrations in micrograms per litre.

		Cd			Cu			Ni			Zn		
Station	No. of observations	Mean	Range	Coeff. var. (%)	Mean	Range	Coeff. var. (%)	Mean	Range	Coeff. var. (%)	Mean	Range	Coeff. var. (%)
J1	9	0.20	0.09–0.62	80	1.30	1.04–1.83	20	2.9	1.7–5.6	45	7.7	4.2–14.7	53
J2	9	0.06	<0.01–0.11	67	0.69	0.37–0.89	22	0.9	0.4–1.9	52	3.2	1.7–8.4	66
J3	9	0.06	<0.01–0.14	67	0.52	0.30–0.54	23	0.9	0.3–1.8	56	2.9	1.4–5.1	52
J4	9	0.05	<0.01–0.10	60	0.55	0.29–0.85	35	0.6	0.2–1.0	53	2.6	0.7–4.3	43
J5	9	0.04	<0.01–0.07	50	0.35	0.14–0.67	46	0.4	0.2–0.6	30	2.0	1.0–3.3	50
J6	9	0.05	<0.03–0.08	40	0.40	0.25–0.68	38	0.3	<0.1–0.5	50	2.2	1.0–3.5	36
J7	9	0.05	<0.01–0.07	40	0.48	0.25–0.79	35	0.3	<0.1–0.6	47	2.6	1.0–6.7	62
J8	9	0.06	0.01–0.12	50	0.58	0.44–0.91	38	0.6	0.3–0.8	30	3.5	2.2–5.8	40
J9	8	0.05	<0.01–0.10	60	0.69	0.45–1.21	38	0.7	0.4–1.2	46	4.2	2.4–7.0	38
J10	9	0.10	0.04–0.20	50	0.89	0.29–1.85	52	1.3	0.8–2.5	50	8.4	2.0–14.1	48
Mean				56			38			46			48

Evidence will be cited in the section on oceanic observations that vertical profiles of the metals studied in the present survey resemble profiles of nutrient salts. One may thus infer that such metals enter into biological cycles and hence may be expected to show seasonal fluctuations in surface waters similar to the nutrient salts in temperate latitudes. Each of the metals at the offshore station J5 was examined for seasonal variation but no such trend was apparent. At the relatively low metal concentration measured in such offshore water, sample contamination will have a proportionately greater influence on the reported value compared with the enriched inshore water. Thus, if any seasonal fluctuations occurred in these waters other factors may well have masked such trends and contributed towards the relatively high coefficients of variation reported at these offshore stations.

There is no other known single investigation that duplicates the entire area of the present study, although reference must be made to the very comprehensive review of trace metals in the waters of this area by Burton and Young (1980). They reviewed the distribution of 27 elements including the early data from the present survey, some of which is now excluded (see Methods). The following comparison of data with other workers is limited to constituents and localities covered by the present investigation. For a fully comprehensive review, Burton and Young (1980) should be consulted. The most extensive survey was that of Preston et al. (1972), which was the precursor of the present exercise but which was biased towards the Irish Sea and western shelf waters. Their 1970 survey of the Irish Sea showed levels broadly comparable with those metals measured during the present investigation. Differences in the method of data presentation makes detailed comparison difficult. Data on dissolved metals in the North Sea were less extensive by Preston et al. (1972). However, Cd values reported by them were markedly higher ($0.3–0.6\ \mu g \cdot L^{-1}$) than those of the present investigation ($<0.075\ \mu g \cdot L^{-1}$) for the area covered by both surveys. The other metals showed broad agreement.

Abdullah et al. (1972) measured Cd, Cu, and Zn in United Kingdom coastal waters of the Irish Sea between 1969 and 1971. Their distribution of Cu and Zn in Liverpool Bay and the Bristol Channel shows fair agreement with the present survey. However, they reported values of over 0.7 $\mu g\ Cd \cdot L^{-1}$ in Liverpool Bay whereas levels were mainly less than 0.2 $\mu g \cdot L^{-1}$ in our investigation. They measured even higher values (4.2 $\mu g\ Cd \cdot L^{-1}$) in the Bristol Channel but Cd was not recorded from that locality during the present survey.

Abdullah and Royle (1974) measured Cu and Zn together with other metals in the water of the Bristol Channel during April and June 1971. They reported generally higher values than the present investigation. They recorded up to 15 $\mu g\ Zn \cdot L^{-1}$ whereas our highest value was 4 $\mu g \cdot L^{-1}$. A maximum Cu value of 1.4 $\mu g \cdot L^{-1}$ measured by us compared with approximately 3 $\mu g \cdot L^{-1}$ reported by Abdullah and Royle (1974) at the eastern end of the Bristol Channel.

In the southern North Sea, Peeters et al. (1973) measured Cu, Ni, and Zn together with other metals off the Belgian coast between 1970 and 1972. Although their survey area was mainly very close to the coastline, their "offshore" values for Zn were comparable with those recorded during the present investigation. Their offshore Cu and Ni values were, however, approximately double the levels reported by us.

Duinker and Nolting (1977) measured Cd, Cu, and Zn (together with Pb) in the eastern part of the southern North Sea during February 1975 as part of an investigation into the relationship between dissolved and particulate phases. Their Cu and Zn values were comparable with the present survey but their Cd levels were higher by a factor of approximately two.

Schmidt (1980) measured Cd, Cu, Mn, and Ni (together with Fe) in the German Bight during May 1974. His data are presented in histogram form without reference to specific localities. However, his distribution of concentration indicates a broad agreement with the present survey for the German Bight for Cd, Cu, and Ni. Our data for Mn are insufficient for that locality to make a valid comparison.

Distribution of particulate trace metals — The amount of data collected on the metal content of the suspended particulate phase is somewhat limited in relation to the information presented on dissolved metals. The term "particulate metal" will be used to refer to that phase measured on the suspended load sample and will include both adsorbed and

truly particulate components. It is immediately apparent that the percentage of particulate metal present in relation to the total was very variable but often in excess of 50% (Table 2). The data as a whole showed a high degree of variability, probably related in part, at least, to the wide regional coverage (spanning coastal to offshore waters) and seasonal variations. However, one must not overlook analytical imprecision at the low metal concentrations often encountered.

Duinker et al. (1979) compared several sampling methods for suspended trace metal analysis and showed a relatively high degree of variability. They emphasized the degree of caution necessary when interpreting such data. Our technique would be expected to measure the acid-labile component but would not include metal bonded into the particulate matrix. It is often considered that the acid-labile fraction is biologically available. However, such an assumption seems somewhat arbitrary and is worthy of further investigation.

For two surveys, data are available on the weight of trace metal associated with a given total weight of suspended material. On these surveys, one in the Irish Sea and the other in the southern North Sea, the statistical relationships between the total amount of suspended particulate material (weight/volume) and the particulate values on a weight/weight and weight/volume basis are given (Table 3). The Irish Sea cruise was carried out during winter months and, thus, the amount of suspended biological material may be expected to be minimal. For Cu, Zn, and Ni a positive correlation is shown between the total weight of suspended material in samples and the content of particulate metal on a weight/volume basis. The correlation is significant to varying degrees of probability and such results are to be expected. The absence of such a relationship with Cd may be due to the low percentage of particulate metal present in that particular survey (Table 2), coupled with a relatively small number of observations. Imprecision of measurements at such low concentrations may well have concealed any correlation. The inverse relationship between the total weight of suspended material and the metal on a weight/weight basis is of greater interest. All four metals showed this correlation, although for the reasons given above, the probability of Cd at 0.1 should perhaps not be treated as significant. The correlation with Zn had the greatest significance (Fig. 4). Although there is a fair degree of scatter, the highest metal concentrations were all associated with the samples having a small suspended particulate load. A similar relationship was noted by Duinker et al. (1979) in water of the Dutch Wadden Sea for Cd, Cu, Pb, and Zn. The reason proposed for the relationship is that proportionately more metal is associated with the finer suspended material compared with the larger bottom-derived particulate matter. Thus, in the less turbulent water one might expect a greater proportion of this finely divided, permanently suspended material. Our own findings appear to substantiate this hypothesis. The results of the present survey in the southern North Sea present a rather different situation. Data for Cu and Zn only are available. There was no correlation between the total weight of suspended particulate material and its metal content on a weight/volume basis. However, the weight of total suspended solid was inversely related to its metal content on a weight/weight basis. At the time of the survey, dense phytoplankton blooms were evident consisting, at least in part, of

TABLE 2. Relationship between dissolved and total trace metal content of water from the North Sea and Irish Sea. Gaps denote particulate values below detection. All concentrations in micrograms per litre (number of observations in parentheses).

		Cu			Zn			Cd			Mn			Ni		
		Dissolved	Total	Particulate/total (%)	Dissolved	Total	Particulate/total (%)	Dissolved	Total	Particulate/total (%)	Dissolved	Total	Particulate/total (%)	Dissolved	Total	Particulate/total (%)
Northern North Sea																
Cirolana 6a/74	Mean	0.22	0.42	52 (6)							0.31	0.40	23 (4)			
July 4–5, 1974	Range	0.15–0.33	0.35–0.53	43–60							0.23–0.46	0.29–0.56	18–30			
	Coeff. var. (%)	33	17	14							35	30	22			
Cirolana 6a/76	Mean	0.20	0.23	19 (75)	1.30	1.62	22 (104)	0.03	0.10	70 (99)						
May 26–June 11,	Range	0.01–0.54	0.02–0.58	4–74	0.08–7.3	0.33–7.7	3–91	<0.01–0.14	0.06–0.20	30–92						
1976	Coeff. var. (%)	65	62	83	78	67	70	64	22	19						
Southern North Sea																
Corella 7/75	Mean	0.55	1.19	51 (30)	2.72	5.87	49 (51)									
May 9–15, 1975	Range	0.12–1.54	0.52–2.70	20–81	1.0–6.1	1.9–12.1	14–80									
	Coeff. var. (%)	47	39	33	44	44	37									
Cirolana 6a/76	Mean	0.30	0.33	12 (16)	1.51	1.89	23 (19)	0.06	0.13	55 (11)						
May 25–June 13,	Range	0.16–0.61	0.22–0.70	3–35	0.77–3.8	0.83–4.3	4–58	0.01–0.13	0.09–0.20	35–84						
1976	Coeff. var. (%)	40	39	62	52	44	55	51	24	27						
Corella 1/77	Mean	0.47	0.76	38 (9)	3.21	5.47	43 (9)									
January 6, 1977	Range	0.14–1.26	0.22–1.98	23–54	1.6–8.2	2.4–12.8	5–88									
	Coeff. var. (%)	70	67	24	63	57	58									
Irish Sea																
Cirolana 1/78	Mean	0.44	0.50	17 (41)	2.64	3.59	30 (44)	0.07	0.08	5 (14)				0.12	0.33	63 (31)
January 9–18,	Range	0.08–1.32	0.14–0.96	4–50	1.0–13.5	1.6–14.6	6–56	0.01–0.23	0.01–0.02	1–15				0.03–0.34	0.09–0.77	22–88
1978	Coeff. var. (%)	48	34	60	98	75	43	111	107	92				43	60	27

TABLE 3. Summary of dissolved and particulate metal concentrations from a survey of the Irish Sea and the southern North Sea (*P* value in parentheses for correlation with total suspended load; NS = not significant).

	Irish Sea (January 9–18, 1978)		Southern North Sea (May 9–15, 1975)	
	Mean	Range	Mean	Range
Dissolved ($\mu g \cdot L^{-1}$)				
Cu	0.44	0.08–1.32	0.55	0.12–1.54
Zn	2.6	1.0–13.5	2.7	1.0–6.1
Cd	0.76	<0.01–0.23		
Ni	0.12	0.03–0.34		
Particulate ($\mu g \cdot L^{-1}$)				
Cu	0.08 (0.0001)	0.02–0.20	0.63 (NS)	0.20–1.52
Zn	0.9 (0.001)	0.3–3.3	3.2 (NS)	0.4–8.3
Cd	0.002 (NS)	<0.001–0.009		
Ni	0.21 (0.001)	0.04–0.60		
Particulate ($\mu g \cdot g^{-1}$)				
Cu	16 (0.02)	1–34	234 (0.001)	23–778
Zn	210 (0.01)	72–445	1158 (0.01)	80–5380
Cd	0.22 (0.1)	0.04–0.56		
Ni	40 (0.05)	4–117		

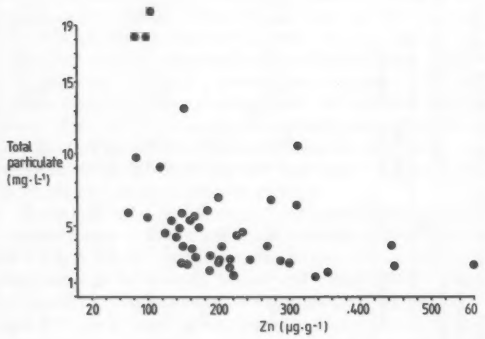

FIG. 4. Relationship between total suspended particulate material and particulate Zn on a weight/weight basis in the Irish Sea during *Cirolana* cruise 1/78 (March 9–18, 1978).

the alga *Phaeocystis*. Morris (1971) measured high concentrations of particulate Cu and Zn associated with blooms of *Phaeocystis* from the Menai Strait adjacent to Liverpool Bay. A similar relationship would account for the present observations. The phytoplankton bloom tended to occur in offshore water where the amount of "heavy" particulate material of inorganic origin was low. Since this planktonic material would contribute little to the total weight of the particulate phase, it is in these samples of low total particle weight that the highest metal contents on a weight/weight basis occurred. Thus, because of the very high amounts of particulate Cu and Zn associated with the plankton bloom, the normal relationship between the weight of total particulate material and trace metal on a weight/volume basis broke down.

It is of interest that the highest concentrations of particulate Cu and Zn measured on the Irish Sea survey were approximately 30 and 500 $\mu g \cdot g^{-1}$, respectively, whereas in the southern North Sea the corresponding values were approximately an order of magnitude greater at 700 and 5000 $\mu g \cdot g^{-1}$, respectively.

An overall comparison of the particulate metal data from Table 2 may be made with the earlier work of Preston et al. (1972). Bearing in mind the degree of variability shown, the two sets of data are in broad agreement except that the percentage of particulate Cu is lower in the present survey (ranging from 12 to 52%) compared with Preston et al. (1972) (>62%). The reason for this anomaly may relate to membrane contamination during the earlier investigation.

Concentrations of trace metals in particles on a weight/volume basis are in broad agreement with the data from the southern North Sea of Duinker and Nolting (1976, 1977). The high amounts of Cu and Zn on a weight/weight basis measured during the *Corella* 7/75 survey were similar to values recorded by Duinker and Nolting (1976) from investigations during September to November of 1973. However, they believed that their values were not caused by the presence of plankton blooms. Duinker and Nolting (1977) reported particulate metal data from another survey during February 1975. Their concentrations of Cu and Zn on a weight/weight basis were more in keeping with the winter Irish Sea levels of the present investigation.

Schmidt (1980) recorded both dissolved and total trace metals in his surveys of the German Bight. Significant quantities of particulate metal were apparent but his method of presentation makes a detailed comparison with the present investigation difficult.

(ii) Other Continental Shelf Waters

Both filtered and unfiltered water samples from this area were analyzed, and in some instances both techniques were

TABLE 4. Distribution of trace metals in the surface water of the continental shelf. All concentrations in micrograms per litre.

Area	No. of observations	Mean	Range	Coeff. var. (%)
		Cd		
A1	19	0.07	0.01–0.17	
A2	9	0.02	0.01–0.03	35
A3	6	0.05	0.04–0.10	58
A4	9	0.03	0.01–0.07	60
A5	2	0.09	0.05–0.13	63
A6	9	0.03	0.01–0.04	43
A7	7	0.01	0.01–0.02	50
		Mn		
A3	16	0.4	0.1–2.3	138
A5	1	0.1		
A6	2	0.2	0.2–0.3	35
A7	12	0.4	0.1–1.7	108
		Cu		
A1	32	0.23	<0.1–0.90	82
A2	16	0.14	<0.01–0.30	64
A3	64	0.30	<0.01–1.80	133
A4	16	0.15	0.07–0.25	47
A5	11	0.37	0.07–1.90	143
A6	11	0.23	0.04–0.30	34
A7	19	0.22	0.10–0.40	45
		Zn		
A1	7	2.1	0.3–4.2	60
A2	12	1.5	0.3–2.0	60
A3	6	1.2	1.0–4.0	78
A4	12	1.3	0.4–2.6	54
A5	5	2.0	0.2–4.4	95
A6	9	1.2	0.5–2.2	50
A7	7	0.6	0.3–0.9	33
		Ni		
A3	4	0.01	0.01–0.02	50
A4	3	0.34	0.08–0.50	73
A6	3	0.18	0.09–0.35	83
A7	6	0.08	0.01–0.16	88

used for comparison. There was no clearly defined difference in the results. Perhaps the amount of "reactive" particulate metal was too small to detect. However, it must be remembered that the organic extraction was carried out on unacidified water at its natural pH. Thus, any acid-labile particulate metal would be expected to remain in the aqueous residue.

Vertical profiles were sampled at some stations. Differences through the water column were sometimes observed although trends were inconclusive. The vertical distribution of metals will be discussed further in the following section and surface observations only will be considered at present.

The trace metal data according to the geographical boxes delineated in Fig. 1 are summarized in Table 4. Data for Mn and Ni are relatively limited for reasons already given. The concentrations of individual metals varied widely. The mean values, however, for most areas were relatively low and were broadly similar to the levels recorded in the offshore zone of the northern North Sea (Fig. 2). One may thus infer that there was little overall evidence of trace metal enrichment from terrestrial sources in spite of the fact that four of the boxes

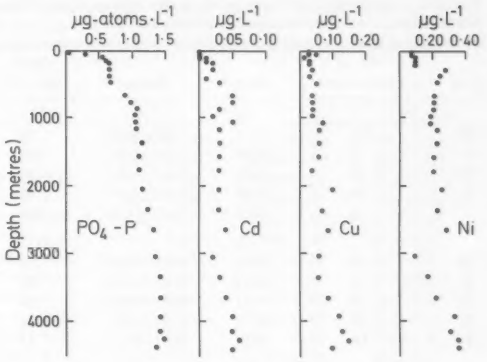

FIG. 5. Vertical profiles of inorganic phosphate, Cd, Cu, and Ni at station 84 in the Bay of Biscay (location reference Fig. 1).

were adjacent to land masses. It is interesting, however, that the highest mean value for Cd and Cu occurred in box A5, adjacent to the northern part of the Irish Sea. The Zn content of water from this box was also relatively high, but data for Ni were not available. By surveying the distribution of radionuclides discharged into the Irish Sea from a nuclear fuel reprocessing plant and their subsequent migration, Jefferies et al. (1982) demonstrated that the predominant flow of water from the Irish Sea passes northwards along the west coast of Scotland. Thus, the metal-enriched water from this area augmented by discharges from the heavily industrialized Clyde would be expected to pass through box A5. Therefore, the relatively high values for Cd, Cu, and Zn in this area may well be partly attributable to sources within the Irish Sea. The relatively low concentrations of metals recorded in the other areas adjacent to land masses are in keeping with the relatively sparsely industrialized hinterlands.

The amount of published data by other workers from the same area is relatively sparse. Values reported by Preston et al. (1972) off the west coast of Scotland are, as one would expect, in broad agreement with the present survey. Kremling and Petersen (1977) measured Cd, Cu, and Zn together with Fe in the water over the Iceland–Faroe Ridge area. The observations made in the top 10 m of water may be compared with our data from box A1. Mean values of 1.5 and 0.06 $\mu g \cdot L^{-1}$ for Zn and Cd compare well with our 2.1 and 0.07 $\mu g \cdot L^{-1}$, respectively, for the same area. Kremling and Petersen's value of 0.57 $\mu g \cdot L^{-1}$ for Cu is, however, double our mean value of 0.23 $\mu g \cdot L^{-1}$, although well within the upper limit of our concentration range.

(iii) NORTH ATLANTIC

Data are presented on surface samples from geographical zones delineated in Fig. 1 and vertical profiles (Fig. 5). All analyses were carried out on unfiltered samples (Table 5). The range of values for each metal (and consequently the coefficients of variation) are again large and resemble the data for continental shelf water (Table 4). In general, the Cd levels are

TABLE 5. Distribution of trace metals in the surface water of the North Atlantic. All concentrations in micrograms per litre.

Area	No. of observations	Mean	Range	Coeff. var. (%)
		Cd		
B	21	0.04	0.01–0.08	50
C	2	0.04	0.01–0.05	100
D	15	0.02	0.01–0.05	50
E	10	0.04	0.02–0.07	50
F	8	0.03	0.01–0.09	100
		Cu		
B	23	0.13	0.01–0.30	69
C	3	0.12	0.05–0.16	50
D	14	0.11	0.03–0.31	64
E	10	0.18	0.07–0.32	44
F	18	0.17	0.01–0.27	47
		Ni		
D	11	0.13	0.07–0.36	62
E	1	0.15		
		Zn		
B	22	1.7	0.4–4.2	65
C	2	1.4	0.6–2.1	79
D	14	1.1	0.4–2.7	72
E	10	1.4	0.5–3.2	64
F	7	0.7	0.3–0.9	29

similar to those measured over the shelf if the "inshore" box A5 is excluded. The mean Cu values for each area of the North Atlantic tend to be lower than the shelf waters, probably due to the absence of some "high" observations measured in the latter investigation. The relatively small number of Ni values from both sets of data make comparison difficult. The range of Zn values for the surface North Atlantic is similar to that for shelf waters, and the mean levels are also similar.

During *Cirolana* cruise 9/75, trace metals together with inorganic phosphate were measured on water samples from vertical profiles in the southeast portion of the North Atlantic. The survey extended from off the shelf to the west of Scotland, southwestwards to the mid-Atlantic Ridge, and then eastwards across the Azores towards the Strait of Gibraltar (Fig. 1). The range of concentrations measured (Table 6) is similar to the surface data listed in Table 5. At several stations, however, vertical profiles of trace metals other than Zn resembled those of inorganic phosphate (Fig. 5). The correlation between inorganic phosphate and each metal at all stations was variable (Table 7) but was most significant for Cd and Ni. Copper and Zn showed poorer correlation with phosphate except with respect to copper at station 84. The most likely explanation must relate to variable low-level contamination of some samples during the cruise from unknown sources (see General Discussion).

In addition to the general trend of higher metal concentrations in the deeper water, at some stations the deepest sample showed a marked elevation compared with the next sample some 100 m above it. Such occurrences are indicated with an asterisk in Table 6 where the metal content of the bottom sample was at least twice the value of the sample above. The most likely explanation would seem to relate to enrichment in the bottom nepheloid layer where perhaps a particulate metal component was influencing the measurement. Variations in the thickness of such a layer coupled with the variable height of the bottom sample above the seabed could be the reason why this effect was not always seen. For a detailed investigation of this phenomenon, samples would be required from much nearer the seabed and at much closer depth intervals than were employed in the present survey.

Several surveys have been conducted into the distribution of trace metals in the North Atlantic. Jones (1975) reviewed post-1963 investigations and Topping et al. (1980) dealt with post-1970 data. Bewers (1979) reviewed surveys conducted in the jurisdictional area of ICNAF. All these reviews concluded that the data showed considerable variability and that it would be difficult to deduce definitive baseline values for any of the metals examined. Over the period of the review, the reported data showed a broad trend for values to fall. The most probable explanation seems to be the progressive improvement of sampling and analytical techniques. The results of the present investigation covered a greater geographical area than any other single survey reviewed and the results were in broad agreement with many of the later investigations. However, specific mention must be made of more recent studies of the trace metal content of oceanic waters. Recently, Boyle et al. (1981) made an extensive review of high-precision data on Cu, Ni, and Cd levels in the surface waters of the North Atlantic and North Pacific. Their data, directly comparable on a regional basis with ours, are rather limited. Their range of Ni values is similar to ours. Their value for Cu is approximately 50% lower than ours but Cd is an order of magnitude lower. However, surface data from our station 84 (Fig. 5) agree very well with values reported by Boyle et al. (1981) from the same area.

Boyle et al. (1976) were the first to show a metal profile in oceanic water which resembled that of nutrient salts. Several workers have subsequently confirmed this relationship for a variety of metals. Bruland et al. (1979) summarized the results of these investigations and presented vertical profiles of Cd, Cu, Ni, and Zn from a station in the Californian Current. They show all four metals to increase in concentration with increasing depth, and in particular, that the distribution of Cd, Ni, and Zn resembles vertical profiles of nutrient salts. They attribute this consistency to the scrupulous care taken to avoid contamination during sampling and analysis. Surveys from the southern part of the North Atlantic of Cd, Cu, and Ni (Bender and Gagner 1976; Moore and Burton 1976) all reported higher values in deep water relative to the surface. Thus, the vertical distribution of these trace metals measured during recent surveys substantiates the findings of the present investigation at those stations where a vertical pattern was evident. The rather random nature of our Zn and Cu data must reflect a greater degree of sample contamination compared with Cd and Ni.

Although Mn and Pb were not measured during this part of the investigations, the findings of two recent surveys are of interest. Bender et al. (1977) surveyed the vertical distribution of dissolved Mn at two stations in the Sargasso Sea. First, their data indicated values mainly less than 0.3 $\mu g \cdot L^{-1}$, about an order of magnitude lower than the results of earlier workers. Second, they did not observe the type of profile recorded by recent workers for the other metals; their values

TABLE 6. The range of Cd, Cu, Ni, and Zn in unfiltered water samples collected during *Cirolana* cruise 9/75 (September–October 1975). All concentrations in micrograms per litre.

Station	Bottom (m)	Sample depth range (m)	No. of samples	Cd	Cu	Ni	Zn
2	2350	0–2212	15		0.05–0.14	0.11–0.33	0.5–2.6
4	3260	0–2742	19		0.05–0.20	0.06–0.30	0.6–3.0
5	3210	0–3165	26	0.02–0.18	0.08–0.25	0.12–0.35	0.4–3.2
6	880	0–841	15	0.01–0.07	0.04–0.58	0.10–0.25	0.4–3.9
7	2040	0–1974	20	0.01–0.08	0.03–0.35[a]	0.07–0.40[a]	0.5–5.0[a]
8	2560	0–2487	21	0.01–0.10[a]	0.05–0.49[a]	0.08–0.34[a]	0.4–3.5[a]
10	420	0–391	9	0.01–0.04	0.06–0.21	0.08–0.18	0.5–3.1
11	4630	0–4503	25	0.01–0.16[a]	0.04–0.56[a]	0.15–0.97[a]	0.7–9.9[a]
12	1720	0–2584	16	0.00–0.13[a]	0.03–0.46[a]	0.10–0.82[a]	0.2–6.8[a]
13	4810	0–4645	27	0.01–0.09	0.05–0.51[a]	0.10–0.42[a]	0.4–9.3[a]
14	1992	0–1899	20	0.00–0.06	0.07–0.12	0.16–0.36	0.6–1.9
15	850	0–819	12	0.00–0.04	0.03–0.10	0.20–0.74	0.5–2.1
16	542	0–501	8	0.00–0.01	0.01–0.12	0.05–0.25	0.4–2.6
84	4650	0–4397	28	0.00–0.06	0.01–0.15	0.08–0.36	0.5–5.3

[a]Bottom sample showed "high" value at least twice the concentration of the sample above.

TABLE 7. Correlation between trace metals and phosphate on vertical profiles at stations in the Atlantic (*Cirolana* cruise 9/75). For locations see Fig. 1. (n = number of observations; r = correlation coefficient; P = level of significance; NS, not significant, $P > 0.01$.)

	Cd			Cu			Ni			Zn		
Station	n	r	P	n	r	P	n	r	P	n	r	P
2	15	0.669	0.005	15	−0.257	NS	15	0.681	0.005	15	−0.527	NS
4	19	0.337	0.1	19	0.487	0.05	19	0.743	0.001	19	0.435	0.05
5	21	−0.309	0.1	21	0.100	NS	21	0.605	0.005	19	0.305	NS
6	15	0.845	0.001	15	−0.172	NS	15	0.774	0.001	15	0.391	NS
7	20	0.424	0.05	19	0.301	NS	20	0.763	0.001	20	0.033	NS
8	20	0.650	0.002	20	0.004	NS	20	0.814	0.001	19	0.339	NS
10	9	0.443	NS	9	−0.208	NS	9	0.596	0.1	9	0.103	NS
11	24	0.701	0.001	24	0.472	0.02	24	0.594	0.005	24	0.321	0.1
12	16	0.798	0.001	16	0.312	NS	16	0.653	0.005	16	0.414	0.1
13	26	0.495	0.01	26	0.387	0.05	27	0.891	0.001	27	0.348	0.05
84	28	0.792	0.001	28	0.723	0.001	28	0.693	0.001	28	−0.262	NS

appeared to be more random in nature but probably related to the water masses present. Third, there was some indication of near-bottom water enrichment resembling the findings of the present survey. Schaule and Patterson (1981) measured the distribution of dissolved Pb in vertical profiles in the northwest Pacific and reported a reverse situation to that encountered during the present investigation. The highest amounts of Pb occurred in the surface waters (approximately 10 $ng \cdot L^{-1}$) but in the deeper water under the thermocline the concentration fell by an order of magnitude. They attributed this pattern to the deposition of atmospheric Pb, which has increased considerably during recent years due to anthropogenic activities. It is of interest that they observed a similar distribution of Mn, a feature not shown so clearly from the Atlantic data of Bender et al. (1977).

General Discussion

The primary aim of these investigations was to assess whether or not the areas surveyed were being measurably enriched by terrestrial discharges of trace metals from anthropogenic sources. The results clearly show such enrichment in coastal waters along those European coastlines surveyed, particularly in the region of major river estuaries. Investigations did not extend sufficiently close to land masses along the North American, Greenland, Icelandic, Scandinavian, or southern European land masses to detect any such influence.

Very broadly, the values measured close inshore were approximately an order of magnitude greater than offshore levels but with the gradient for Mn somewhat larger. Such changes in concentration were confined to a relatively short distance normal to coastlines, and the central North Sea, for example, was almost indistinguishable from the open Atlantic with respect to trace metal concentration. Thus, for the metals analyzed here, together with the surveys cited, there is little evidence of measurable enrichment in oceanic water from anthropogenic sources. The vertical patterns of distribution resemble those of nutrient salts and hence suggest natural biological mobilization processes. Lead, however, and possibly Mn, are the exceptions where surface enrichment has been

demonstrated presumably from atmospheric deposition far from terrestrial sources.

Cambray et al. (1979) have estimated that broadly similar quantities of Cd, Cu, Ni, Mn, and Zn enter the North Sea via direct rainfall compared with discharge from the River Rhine. Moreover, approximately three times as much Cu and Pb is deposited from the atmosphere compared with the Rhine source. No direct information is available on the rainfall deposition of trace metals into oceanic water although the data of Schaule and Patterson (1981) would suggest that the atmospheric input of Pb and possibly Mn must be considerably higher than the other metals, at least in their area of study. The distribution of trace metals in surface waters alone cannot be used to assess gross input values. Atmospheric deposition may far outweigh fluvial inputs, but because of the vast dilution factor in oceanic water, coupled with limits of detection, such inputs may be undetectable.

Although not examined in detail, our data show the importance of suspended particulate trace metals in shelf waters. Often, there was more metal in this phase than in filtered water. Thus, any study of metal fluxes or amounts present in the context of pollution investigations should take both dissolved and particulate components into account.

In general, our data showed fair agreement with the results of other workers. We have drawn attention to the trend for reported trace metal concentrations to decrease over the last decade and have attributed the phenomenon primarily to improvements in sampling and analytical techniques, particularly by reducing sources of contamination. There were no instances in which the more elevated inshore levels in our results were markedly higher than those of any other investigation.

Throughout the period, a series of international intercalibration exercises for trace metals in seawater was conducted, and the unit that provided analytical support for the present survey actively participated. The ICES Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic has sponsored several such exercises. Standard trace metal solutions and shelf seawater have been intercalibrated (Jones and Baker 1983) as have more offshore waters (Bewers et al. 1981). A similar interest in intercalibration has been maintained within the Joint Monitoring Group of the Oslo and Paris Commissions, and they have requested ICES to conduct exercises on their behalf. One such exercise has been carried out on Cd (Thibaud 1981). Future ICES programs have been planned with a greater emphasis on sampling and storage, and their rationale has been discussed in Topping et al. (1980). The intercalibration series as a whole has shown a better degree of agreement during the later exercises with a progressive reduction in the number of very anomalous results. The increasing number of high-precision measurements of trace metals in oceanic water that have appeared during recent years where coherent vertical patterns have become evident for the first time substantiates this trend. Goldberg (1981) has recently written of the "revolution" that has occurred during the last decade in trace metal analysis following Patterson's work on Pb in seawater. Now, for the first time, credible data are being reported on oceanic trace metal concentrations.

The validity of data from the present series of surveys must be viewed in the light of the abovementioned trends. Evidence has been cited that our oceanic trace metal data are broadly comparable with the most recent published values but that the degree of precision and hence the clarity of vertical differentiation is not as high as desirable. Samples were taken during multipurpose cruises, and the facilities to collect and process the water under rigorously controlled conditions were not available at the time. However, one must relate the sampling and analytical facilities available to the requirements of the survey. Clearly, if the prime aim of an investigation is a fundamental study of metal fluxes in oceanic water, then the types of techniques described by Bruland et al. (1979), for example, must be adopted. However, such facilities are not readily available to all laboratories involved in seawater analysis. If only contaminated inshore water is being analyzed, then the highly sophisticated system vital for oceanic water is not as necessary although much care is still required. The aims of the present survey fall more within this latter group. The fact that our offshore values fall away to approximate oceanic levels gives confidence in the validity of the inshore measurements.

Topping et al. (1980) believe that as yet there are insufficient reliable data available from the North Atlantic to assess baseline values. The situation is somewhat less acute in coastal waters where there are more observations, but the greater degree of natural variability in such areas makes comparisons difficult. Ideally, we require a set of proven techniques both of sampling and analysis for oceanic and inshore water such that data produced by different groups may be truly comparable. To maintain uniformity, regular intercalibration must also be a feature of such a plan. The study of trace metals in seawater over the last decade has moved significantly towards this situation although the ultimate goal has yet to be achieved.

Acknowledgment

We wish to thank the Deutsches Hydrographisches Institut for providing facilities to collect water samples onboard the research vessel *Meteor*.

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Potential Anthropogenic Influences on Trace Metal Distributions in the North Atlantic[1]

P. A. YEATS AND J. M. BEWERS

Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

YEATS, P. A., AND J. M. BEWERS. 1983. Potential anthropogenic influences on trace metal distributions in the North Atlantic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 124–131.

This paper discusses the application of geochemical understanding of an estuarine and marginal sea environment to an assessment of marine contamination by trace metals. The estuaries and Gulf of St. Lawrence are used as an analogue of a section of the nearshore and continental shelf environment in which metal fluxes, in both dissolved and particulate form, can be estimated. Estuarine and nearshore removal of 99% of the particulate matter, >97% of the particulate Fe and Mn, and 25–50% of the Ni, Co, Cu, Zn, and Cd discharges are indicated. The dissolved Mn efflux is augmented slightly within the gulf. A generic coastal zone model is used to examine the magnitude of exchanges between particulate and dissolved metal phases during transport between the freshwater and deep marine environments. This model is also used to compare global river discharges with metal accumulations in nearshore and pelagic sediments. The current influxes of Zn and Cd to the ocean greatly exceed their rates of sedimentation. The imbalance for Zn may merely be due to limited and inaccurate measurements of Zn in continental runoff. The Cd imbalance, however, appears to be real and reflects a major increase in the mobilization of this metal. Finally, oceanic metal distributions are examined for evidence of contamination of the northwest Atlantic by metals of anthropogenic origin.

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On trouvera dans l'article qui suit une analyse de l'application de nos connaissances géochimiques d'un environnement estuarien et marginalement marin à l'évaluation d'une contamination marine par métaux en traces. Nous avons utilisé des estuaires et le golfe du Saint-Laurent comme analogue d'une section de l'environnement du voisinage de la côte et du plateau continental dans lequel peuvent être estimés les flux de métaux, tant dissous que particulaires. Nous constatons que 99 % de la matière particulaire, >97 % de Fe et de Mn particulaire, et 25 à 50 % des apports de Ni, Co, Cu, Zn et Cd sont enlevés des milieux estuariens et côtiers. L'effluent de Mn dissous est légèrement plus élevé à l'intérieur du golfe. Un modèle générique de la zone côtière a servi à étudier l'ampleur des échanges entre les phases particulaire et dissoute des métaux lors du transport entre l'eau douce et les profondeurs de la mer. Ce modèle a servi également à comparer le débit global des rivières avec l'accumulation des métaux dans les sédiments du voisinage du rivage et pélagiques. Les apports de Zn et Cd par les courants en direction de l'océan dépassent de beaucoup leurs taux de sédimentation. Ce déséquilibre de Zn peut être simplement le résultat de mesures limitées et imprécises de ce métal dans le ruissellement continental. Par contre, le déséquilibre de Cd semble réel et reflète une importante augmentation de la mobilisation de ce métal. Finalement, nous avons voulu découvrir des preuves de contamination de l'Atlantique nord-ouest par des métaux d'origine anthropogénique en examinant la distribution océanique des métaux.

Received March 19, 1982
Accepted November 17, 1982

Reçu le 19 mars 1982
Accepté le 17 novembre 1982

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6854)
Imprimé au Canada (J6854)

THE sheer volume of the ocean provides it with a very large capacity to absorb increased influxes of chemicals without marked changes in the ambient pelagic concentrations of such chemicals being evident. This is particularly true for chemicals, such as trace metals, that are already present in the

ocean as a consequence of natural processes. Trace metals have oceanic residence times typically between 10^2 and 10^5 yr, and these times are long enough to ensure relatively slow rates of equilibration with new injection conditions. During periods of non-steady-state conditions, as would occur following significant increases in the oceanic influx of a metal as a result of anthropogenic activities, the spatial distribution of the metal in the ocean would differ from that prevailing under purely natural conditions. However, the limitations imposed by the precision with which determinations of most trace metals in seawater can be effected, and the necessity of estimating their likely natural distributions, present formidable restrictions upon the use of direct measurements for detecting such changes. Only in cases where substantial changes in the influx of generally biologically inactive metals have occurred can direct measurements be reliably used for these purposes. Such a situation applies to Pb and several radionuclides of artificial origin that have been introduced to the world ocean as a consequence of nuclear weapon explosions. For most other metals, either the changes in their oceanic injection rates are insufficiently pronounced or their rates of internal cycling are so rapid that it is not possible to postulate the degree to which their present distributions reflect anthropogenic influences. We therefore have to seek alternative approaches to gauging the extent of oceanic contamination that may be based predominantly upon indirect measurements.

Progress in the study of metal distributions and behavior in the deep ocean has been relatively rapid during the last decade. This progress has been largely the result of advances in sampling and analytical techniques for the determination of metals in seawater. The nutrientlike vertical profiles of Zn and Cd, which reflect the involvement of these metals in biological uptake and regeneration processes, are some of the more significant results of recent work. Surface enrichments suggestive of aeolian injections have also been observed for some metals. It is a striking commentary upon such progress that there now exists a better understanding of the distributions and behavior of several metals in the deep ocean than of their rates of influx through river runoff and atmospheric precipitation. More balanced attention to the composition of rivers and atmospheric deposition is urgently required to redress this situation. However, we can and intend here to use the best information that is available regarding the riverborne fluxes of metals, together with information on processes in the coastal zone that influence the fluxes of metals into the deep ocean basins, to gain an appreciation of the likely extent of pelagic contamination resulting from human and industrial activities.

Metal Transport Through the Coastal Zone

The transport of metals through the coastal zone can be visualized as part of the progression from rivers, through the estuarine and continental shelf environments, to the deep ocean. The coastal zone is defined here as the estuarine and continental shelf waters and sediments. Exchanges of metals occur between the coastal zone and the adjacent continent, the overlying atmosphere, and deep marine environments although the net flow of metals is generally from the continents to the deep ocean. Much attention has been focussed on the behavior of metals in estuaries but it is only really for Fe and Mn that any universal aspects of behavior have been established. Less attention has been paid to the continental shelf environment both in terms of metal behavior and the modes of metal exchange between the continental shelf and the deep marine basins. Estuarine processes will, however, continue to affect transfer across the continental shelf and it is therefore unwise to infer that the export of metals from estuaries corresponds to the influx to the deep ocean. The fact that concentration changes in the offshore are more subtle than in estuaries introduces difficulties in their study but should not result in the neglect of metal behavior in such regions.

Estimates of metal fluxes in the discharges of several major rivers are available. Such estimates have been made for the Amazon (Gibbs 1977), the Mississippi (Trefry and Presley 1976), and the Yukon (Gibbs 1977). An important survey of the metal content of suspended material carried by major world rivers has also been published by Martin and Meybeck (1979). In recent work on the composition of the St. Lawrence River (Yeats and Bewers 1982), we found that there exists a great deal of similarity in the dissolved and particulate metal content of several major rivers. We used this similarity to make hopefully realistic estimates of the discharge of trace metals in dissolved and particulate forms within global river runoff by scaling the composition of different major rivers.

The deposition of metals from the atmosphere into the coastal zone is, by comparison, poorly known. Cambray et al. (1975) estimated the influx of trace metals from the atmosphere to the North and Clyde seas. Topping (1974) compared the influxes of metals from various sources to the Clyde Sea and concluded that atmospheric deposition was a major contributor to metals in that sea. A similar conclusion was reached by Windom (1979) for the southeastern United States coastal zone. Since these two independent estimates of the depositional fluxes per unit area agree within an order of magnitude, they can provide a very rough estimate of deposition for other coastal areas. However, direct measurements for other coastal regions are urgently required before any large-scale estimates of atmospheric transport into the coastal zone can be made.

The exchanges at the coastal zone–ocean boundary are undoubtedly the greatest unknown in the mass-balance equation for the coastal zone. Whilst the composition of the marine source water becomes an increasingly stable quantity with distance from freshwater sources, the actual discrimination between the marine (landward flowing) water and the mixed (seaward flowing) water becomes increasingly difficult. In most cases it is not possible to identify unambiguously these individual water flows on the outer continental shelf. Marine source water may appear on the shelf only as a complicated and varying mixture of oceanic water masses, or only intermittently, for example as a result of periodic upwelling. Furthermore, mixed water may be flowing predominantly along the coast rather than perpendicular to it. Only where oceanographic conditions are suitable and reliable hydrographic (physical oceanographic) information is available can any attempt be made to distinguish between these counterflows. In general, the closer one approaches the estuarine zone the easier this distinction becomes, but as we have stated earlier,

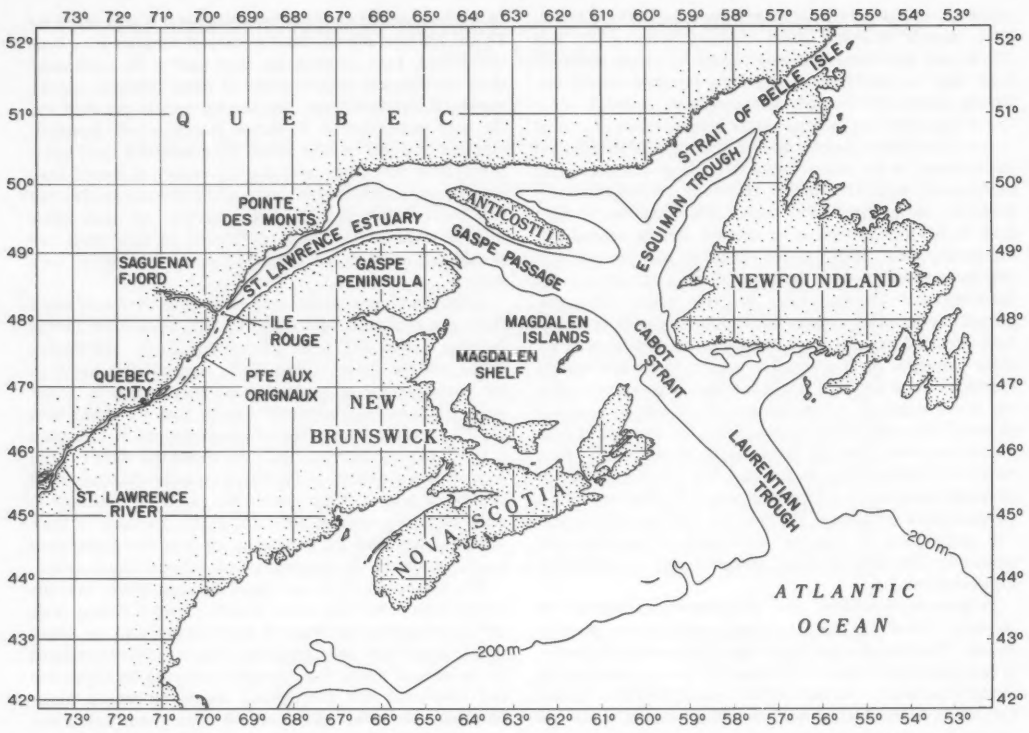

FIG. 1. The Gulf of St. Lawrence.

we believe it important that some estimate of the cumulative effect of processes in both estuarine and continental shelf environments be gained, and this conviction in turn demands that we examine the composition of landward and seaward flowing waters as remotely as possible from freshwater sources.

Gulf of St. Lawrence Model

The Gulf of St. Lawrence can be used in this context as an analogue of the continental shelf, since the composition of the inflowing and outflowing saline waters can be determined at the seaward boundary of the gulf at Cabot Strait. The Gulf of St. Lawrence (Fig. 1) has many characteristics that are similar to those of a section of continental shelf. Not only has the gulf a large area (approximately 250 000 km^2) but its water depths are comparable with those on the adjacent continental shelf. About 20% of its area has water depths exceeding 300 m, while its estuarine and shallower regions contain typical water depths of 20–60 m. The waters of the gulf remain stratified throughout the year, and only in the shallower regions does the seasonal thermocline penetrate to the sediment–water interface. The biggest single contributor of freshwater is the St. Lawrence River which discharges approximately 14 000 $m^3 \cdot s^{-1}$ (4.4×10^{14} $L \cdot yr^{-1}$) into the western extremity of the system. The majority (71%) of the entire freshwater inflow to the gulf is derived from rivers to the west of Pointe des Monts. The sediments in the deeper parts of the gulf, particularly in the Laurentian Trough, are predominantly fine clays, whilst the nearshore sediments in the peripheral regions of the gulf and around Anticosti Island are mostly coarser materials including gravels, sands, and sandy muds (Loring and Nota 1973). This mixture of sediment types is similar to that on the adjacent Scotian Shelf where relict sands underlay the shallower inshore areas and finer silts and clays occupy the deeper depressions. The main flow of fresher surface water is from the St. Lawrence Estuary, along the Gaspé Peninsula, and across the Magdalen Shelf with the resulting mixed water flowing out through the southern side of Cabot Strait. The transit time for freshwater to Cabot Strait is 3–4 mo whereas the overall residence time of water in the entire system is closer to a year (Trites (1970). At Cabot Strait, and at several other sections in the gulf, the outflowing mixed water and inflowing marine water can be readily identified, and the magnitude of flow and water fluxes have been estimated (El Sabh 1975). Exchanges of water through the other connection between the gulf and the North Atlantic, at Belle Isle Strait, are relatively small and for the purposes of simplistic budget calculations can be neglected. Thus, the Gulf of St. Lawrence is a coastal sea that in many ways is

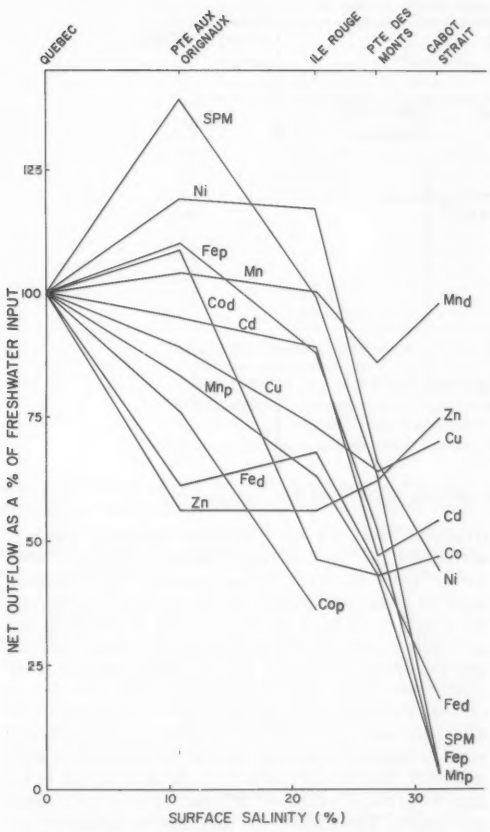

FIG. 2. Plot of net metal effluxes versus salinity at various sections in the Gulf of St. Lawrence for particulate (subscript p) and dissolved (subscript d) Fe and Mn, and total Co, Ni, Cu, Zn, Cd, and suspended particulate matter (SPM).

analogous to a section of continental shelf with the advantage that processes and fluxes within the gulf can be conveniently modelled.

The first use of a geochemical model for the entire gulf was that made by Sundby (1974) in an attempt to construct a budget for suspended particulate matter (SPM). The same approach was used later by Coote and Yeats (1979) to determine the cycling of nutrients in the system and the relative importance of various nutrient sources and sinks. We have studied the distribution of metals in the gulf since 1972 and the results have been used to construct box models to examine the fluxes of metals within the area (Bewers and Yeats 1977, 1978, 1980). The physical oceanography upon which these models were based was derived from contemporary knowledge of the estuary and Gulf of St. Lawrence, while water fluxes were calculated on the principles of mass and salt conservation. They are therefore quasi-steady-state models that only attempt to make approximations to the real conditions in the system over relatively small intervals. The metal characteristics of the inflowing and outflowing water masses at the boundaries of each box were estimated from direct measurements. At Pointe des Monts and Cabot Strait the flows were characterized by direct measurements in the corresponding cross-sections using physical oceanographic data as a basis for identifying inflowing and outflowing waters. In the estuarine region, the average salinities of the inflowing and outflowing saline water masses were determined and the corresponding metal concentrations interpolated from metal–salinity relationships. This procedure results in the establishment of a hydrographic, rather than a geographic, boundary for the estuarine region.

The results of the various box models applied to the Gulf of St. Lawrence are most easily summarized in a plot of net metal efflux from each section, expressed as a percentage of the riverine influx, against surface salinity of the section as shown in Fig. 2. This figure is based on data presented in Bewers and Yeats (1977, 1978), with the upper estuary section divided in two by an additional section at Pointe aux Orignaux. In the upper estuarine region (Quebec City to Ile Rouge), SPM export increases to a maximum near Pointe aux Orignaux, where a typical estuarine turbidity maximum is present. At Ile Rouge the SPM export is equal to the amount entering the estuary in riverine and marine source waters, implying that there is no net loss or gain of suspended matter within the upper estuary. Although the SPM flux at Pointe aux Orignaux is increased by 40%, the particulate Fe flux increases by only 5%, whilst those of particulate Mn and Co are reduced. At Ile Rouge the particulate Fe, Mn, and Co outflows are all attenuated compared with the metal influxes. Since SPM is conserved, the removal processes must be more complex than straightforward sedimentation of particulate material.

In the lower St. Lawrence Estuary and the Gulf of St. Lawrence, SPM is extensively removed. The net efflux of SPM at Cabot Strait is only 1.2% of the total river inflow. Particulate Fe and Mn are also substantially removed from the water, their outflows being 2.4 and 2.7% of their respective influxes. Of the dissolved metal fractions, Fe shows the greatest removal with the net efflux of dissolved Fe at Cabot Strait being only about 20% of the river influx. The net effluxes of total Co, Ni, Cu, Zn, and Cd are in the range of 50–75% of their influxes in freshwater, while the dissolved Mn flux is augmented in relation to the dissolved Mn influx from rivers.

It is evident from Fig. 2 that SPM and the associated particulate metals are removed more rapidly outside the highly energetic estuarine regime. Most of the total Co, Cu, and Zn are removed within the estuarine region of the system. Subsequent changes in efflux within the Gulf of St. Lawrence downstream of Ile Rouge are relatively small. Ni and Cd removal shows the opposite trend, being relatively unaffected by processes in the upper estuary, but with significant removal in the lower estuary and gulf. Dissolved Fe is the only other element whose efflux is significantly reduced in the gulf itself. In this case, the net outflow at Ile Rouge is approximately 70% of the river flux, while at Cabot Strait it is only 20%. Estuarine precipitation of dissolved Fe, accompanied by

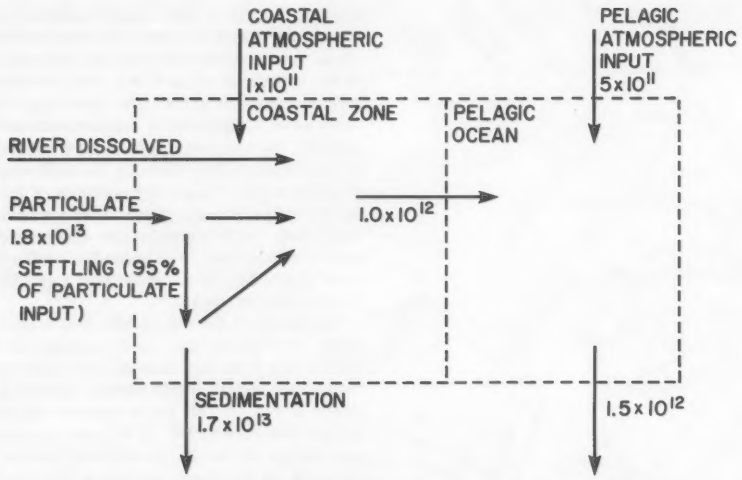

FIG. 3. Generic coastal zone model illustrated with particulate matter fluxes (kilograms per year).

precipitation of Co, Cu, and Zn, is evidently occurring in the upper estuary. Downstream in the gulf, Fe removal continues either by continued inorganic precipitation or by biological uptake. A biological removal mechanism in the gulf is most likely for Ni and Cd. Whatever the mechanisms, continued removal of Fe and some of the other metals in the more quiescent regions of the system is an indication of the importance of similar flux reductions in the continental shelf areas of the world ocean.

It should be stressed that all the above conclusions are derived from steady-state models applied to the metal flows through the gulf. The input data for these models were derived from a particular season of the year, that of high spring–summer runoff, and therefore the results of the application of the models give only a quasi-instantaneous picture. Nevertheless, the general trends of the results might be expected to apply, in rough terms, to a typical section of continental shelf. Water residence times on typical continental shelf regions are similar to that for the Gulf of St. Lawrence, and therefore we turn now to an examination of the probable consequences of estuarine and continental shelf processes upon the fluxes of runoff-derived metals into the deep ocean generally.

A Generic Model of Trace Metal Transport Through the Coastal Zone

It is not possible to model typical continental shelf regions in the same manner as that carried out for the Gulf of St. Lawrence because the fluxes cannot usually be adequately characterized, especially those at the offshore boundary of the continental shelf. Some insight into the processes of metal removal on continental shelves can be derived from a comparison of dissolved and particulate metal contents of river discharge with the composition of continental shelf and pelagic sediments. If we assume that the total suspended particulate discharge of rivers is 1.8×10^{13} kg·yr^{-1} (Holeman 1968) and that 95% of this particulate matter is sedimented on the continental shelves (Broecker 1974; Bewers and Yeats 1977), we can generate a model for trace metal fluxes across the global continental shelf (i.e. through the world coastal zone) as shown in Fig. 3. Dissolved and particulate metals enter the coastal zone by riverine transport and atmospheric deposition and are either retained in the coastal zone by nearshore sedimentation or leave it through offshore water transport. The net metal sedimentation rate in the coastal zone can be estimated from the concentration of a metal in nearshore sediments and the rate of nearshore sedimentation. The flux of metals from the coastal zone to the deep ocean basins will be the difference between these inputs and outputs. The residual flux may then be divided by the pelagic sedimentation rate to yield a predicted metal concentration in deep-sea sediments (Table 1). These calculations give reasonable predictions for the pelagic sediment concentration of Al, Fe, Mn, Co, Ni, and Cu. This would imply that the present-day fluxes of these metals are roughly compatible with the rates at which continental shelf and pelagic sediments have been supplied with these metals over recent geological history. Any augmentation of the runoff concentrations of these metals by anthropogenic activity must therefore have been relatively small. These calculations have ignored potential inputs of metals through volcanic processes. Recent studies in the vicinity of Pacific Ocean spreading centres indicate that a large flux of Mn is issuing from hydrothermal vents. These additional inputs will be at least partially compensated for the elevated Mn content of metalliferous sediments. It is also a possibility that the Mn flux in runoff is substantially larger than that in precultural times, as concluded by Mackenzie and Wollast (1977).

The predicted pelagic sediment concentrations of Zn and Cd are considerably higher than the observed concentrations by factors of 10–15 and 25–65, respectively. These differences greatly exceed any uncertainty in the composition of

TABLE 1. Results of the generic coastal zone model.

Component	Global river discharge flux ($kg \cdot yr^{-1}$)	Net efflux from the coastal zone ($kg \cdot yr^{-1}$)	Proportion redistributed in the coastal zone (%)	Pelagic sediment concn.[a] Predicted	Observed
SPM	1.8×10^{13}	1.0×10^{12}	—	—	—
Al	1.4×10^{12}	7.8×10^{10}	0	7.8%	8.0%[b]
Fe	9.2×10^{11}	5.5×10^{10}	0.2	5.3%	5.8%[c]
Mn	2.2×10^{10}	7.9×10^{9}	31	5600	4000,[d] 12 500[e]
Co	3.0×10^{8}	7.8×10^{7}	21	61	38,[d] 116[e]
Ni	1.5×10^{9}	2.3×10^{8}	8	180	72,[d] 293[e]
Cu	2.5×10^{9}	5.8×10^{8}	34	410	130,[d] 570[e]
Zn	5.4×10^{9}	2.8×10^{9}	46	1900	130[d]
Cd	3.0×10^{7}	1.3×10^{7}	31	8.5	0.5[f]

[a]Grams per kilogram unless otherwise stated.
[b]Value for sedimentary rocks.
[c]Average pelagic clay after Rosler and Lange (1972).
[d]Atlantic pelagic sediments after Chester and Aston (1976).
[e]Pacific pelagic sediments after Chester and Aston (1976).
[f]Average oceanic sediments after Simpson (1981).

marine sediments, and we therefore must examine other possibilities to explain them. The fluxes of metals from world rivers have been based upon the flux and composition of suspended matter in a large number of rivers reported by Martin and Meybeck (1979). However, the dissolved metal fluxes have been based upon the results from a small number of rivers and in the cases of Zn and Cd, solely on the fluxes from the St. Lawrence and Mississippi rivers. The drainage basins of both of these rivers are fairly heavily industrialized and populated, and it is therefore possible that the apparently high influxes of Zn and Cd to the world ocean are an artifact of the abnormal composition of these two rivers. A reduction of both the dissolved and particulate Zn discharge by a factor of 2–3 would bring this influx into steady-state balance with the flux of Zn to marine sediments. Such an overestimate is not unreasonable given the uncertainties in trace Zn determinations and the variability in metal discharges from rivers, but it should be noted that some rivers, such as the Rhine (Duinker and Nolting 1978), contain considerably higher Zn levels than those in the St. Lawrence or Mississippi.

Cd is much more seriously out of balance. The dissolved Cd influx would have to be reduced by at least a factor of 5 and the particulate flux by a factor of 10 to bring the predicted pelagic sediment concentration down to measured levels. These reductions would require that the average dissolved Cd concentration in rivers be approximately 20 $ng \cdot L^{-1}$ and in riverine suspended matter be approximately 0.15 $\mu g \cdot g^{-1}$. A few years ago the discrepancy between the influx and efflux of Cd to the world ocean could be attributed to inaccurate measurements of the composition of river waters. However, a good deal of recent information on the Cd composition of rivers exists which is based upon the application of more precise and accurate sampling and analytical technology. Such information (Trefry and Presley 1976; Nurnberg et al. 1976; Duinker and Nolting 1978; Poldoski and Glass 1978; Duinker et al. 1980; Klinkhammer and Bender 1981; Grant et al. 1982; Yeats and Bewers 1982) supports the idea that there exists a great deal of spatial heterogeneity in Cd concentrations in river water. Although the highest Cd concentrations appear to occur in heavily populated and industrialized rivers, the extent to which Cd concentrations are a direct reflection of specific anthropogenic inputs remains to be determined. Nevertheless, these observations tend to support the results of reviews of Cd in the marine environment (Simpson 1981), and Cd use and dissemination in Canada (D. MacGregor, Environmental Impact Directorate, Environment Canada, Ottawa, personal communication) that indicate that the rates at which Cd is being mobilized by man are now comparable with the natural hydrologic fluxes of the element. The distribution of Cd in the deep ocean remains insignificantly affected by increased influxes because of its rapid rate of recycling in the surface layers. Cd is intimately involved in biological incorporation and regeneration cycles in the surface ocean such that its residence time in surface waters is quite short, less than a year in Pacific surface layers where the most rapid Cd recycling occurs (Knauer and Martin 1981). Thus, the refluxing of Cd through the upper layers of the ocean as a consequence of biological activity is much larger than the influx of the metal from rivers. The deep ocean residence time is relatively long, about 10^5 yr (Bewers and Yeats 1977), and it will therefore take considerable time before any pronounced concentration or distributional changes occur there. It would be mere speculation to answer the question as to whether the apparent Zn imbalance reflects similar increased mobility as a result of anthropogenic activity. The determination of Zn in seawater is somewhat more difficult than for Cd and its biological involvement seems to be just as profound as Cd, although over comparatively deeper regenerative cycles (Bruland 1980). Therefore, we must await further, more reliable measurements of Zn in rivers before being able to determine whether the metal shows similar spatial heterogeneity in runoff to that of Cd.

Another interesting facet of the application of the generic model to contemporary data evolves from a comparison of the differences between the metal content of riverborne suspensoids and that of nearshore sediments. In most cases the

metal content of riverborne particulate material is higher than that of coastal sediments. This implies that some change in the particulate metal concentrations is occurring within the coastal zone such that the material ultimately deposited in the sediments has lower trace metal content than the riverborne particles. This redistribution may occur by a variety of processes including dilution by marine particulates, size sorting of river-derived particles, estuarine desorption of metals, and diagenetic release of metals from the sediments. The extent of redistribution in the Gulf of St. Lawrence is expressed in Table 1 as a fraction of the metal sedimentation in the gulf. While there is negligible redistribution of Al and Fe and very limited redistribution of Ni, the other metals (Mn, Co, Cu, Zn, and Cd) are considerably redistributed and remobilized in the coastal zone. This emphasizes the rather metal-specific nature of the processes that determine the proportion of a given metal that is able to survive nearshore sedimentation and succeed in reaching the deep ocean basins before sedimentation occurs. Extensive release of Mn from gulf sediments (Yeats et al. 1979) points to diagenetic remobilization of Mn from newly deposited river-derived particles within the surficial sediments as the major mechanism of Mn remobilization within the gulf. Similar remobilization of Cu from sediments has also been suggested (Boyle et al. 1981). Dissolution of Mn and Ni from particles in the upper estuary is also indicated by the flux calculations illustrated in Fig. 2. Preferential settling of coarser particles with lower trace metal content is likely to be an important enrichment mechanism for Fe and several of the other metals, such as Cu and Zn, that are commonly enriched in the finest particles.

Oceanic Metal Distributions

The wide variety of physical, chemical, and biological processes affecting metal distributions in the pelagic ocean will make it difficult to detect the effects of anthropogenic inputs on oceanic metal concentrations. Nevertheless, the rather large augmentation of natural inputs for some metals, notably Cd and possibly Mn and Zn, may lead to noticeable effects on oceanic distribution, particularly surface concentrations.

In the surface mixed layer of the Sargasso Sea, Cd concentrations are reduced to as low as 0.002 $nmol \cdot L^{-1}$ and Zn to 0.06 $nmol \cdot L^{-1}$ as a result of uptake of these metals by microorganisms (Bruland and Franks 1981). In the Pacific Ocean, similar surface Zn and Cd levels are observed (Bruland 1980). On two of five stations further north in the Atlantic, however, very shallow samples (less than 25 m) show elevated Zn levels with concentration minima at 50–100 m. As the coastal zone is approached the surface concentrations of Cd, and in one case Zn, increase dramatically (Bruland 1980; Boyle et al. 1981; Bruland and Franks 1981). The vertical profiles of Ni are also related to those of the nutrients; however, the surface concentrations are not reduced to the extent that Cd and Zn are. The residual surface Ni concentration in the North Atlantic, 2.0 $nmol \cdot L^{-1}$, is very similar to the surface concentration observed in the eastern Pacific Ocean (Bruland 1980). As with Cd, Ni concentrations have been shown to increase towards the coast. For all of these metals, biological processes are effectively removing terrigenous inputs including any anthropogenic Cd from the surface mixed layer. Because of the biological cycling, any metal buildup may be expected to occur at the depth of maximum nutrient and associated metal regeneration rather than in the surface waters. Insufficient data are yet available to investigate this possibility. There is thus little indication of surface buildup due to aeolian inputs of these metals, except possibly for Zn in some locations. Elevated concentrations from other inputs (or remobilization in coastal sediments) are restricted to areas near the continental shelves. The extent to which these elevated levels are attributable to anthropogenic activity is unknown.

Cu and Mn present a rather different picture. Their distributions are less affected by biological processes and as a result, they do not have nutrientlike depth profiles. Elevated surface concentrations that reflect aeolian inputs or river runoff have been observed in several cases. In the Pacific Ocean, direct correlation between ^{210}Pb (an indicator of aeolian inputs) and surface Cu (Boyle et al. 1977) and Mn (Klinkhammer and Bender 1980) concentrations has been observed. In addition, Cu and Mn concentrations increase from the central ocean areas towards the continents, and surface concentrations are higher in the northwest Atlantic than in the Pacific (Bruland 1980; Boyle et al. 1981; Bruland and Franks 1981). These observations are a reflection of greater runoff and aeolian inputs to the Atlantic compared with the Pacific. Again, anthropogenic effects cannot be distinguished from the natural.

Particulate Fe and Mn and dissolved and particulate Al also have elevated concentrations at the surface decreasing with depth to minima at 200–500 m that are indicative of aeolian inputs (Hydes 1979 for Al). Little is known, however, about geographical variations in the surface concentrations. Dissolved Fe has not been extensively studied, but the few profiles that are available show little indication of surface layer enrichment. Evidence of the high dissolved Fe input from rivers is thus absent in the central ocean basins. Fe is removed from the surface layer either by a continuation of the inorganic processes predominant in estuarine and nearshore regions or by biological removal in the deep sea.

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Remobilization of Metals from Polluted Marine Sediments[1,2]

CARLTON D. HUNT AND DEBORAH L. SMITH

Marine Ecosystems Research Laboratory, Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881, USA

HUNT, C. D., AND D. L. SMITH. 1983. Remobilization of metals from polluted marine sediments. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 132–142.

The transition metals Cu, Pb, Fe, Mn, and Cd were examined to estimate short- and long-term release rates from highly contaminated sediments and to compare this release with present metal flux into an ecosystem. The concentration of Cu and Pb increased in the water column over contaminated marine sediments when these sediments were isolated from metal and organic carbon sources and held in large (13 m^3) marine microcosms. During the summer and early fall, Cu concentrations increased by a factor of 3 relative to the concentration in microcosms containing slightly polluted and uncontaminated sediments. Mass balance calculations indicate that 840 and 21 $\mu mol \cdot m^{-2} \cdot yr^{-1}$ Cu and Pb, respectively, were mobilized and exported from the microcosms with highly contaminated sediments, while less-contaminated sediments lost 120 $\mu mol\ Cu \cdot m^{-2} \cdot yr^{-1}$. Iron and Mn were not exported from the microcosms. In the absence of high sedimentation rates and high bioturbation rates, the diffusive loss of Cu and Pb may be sufficient to return the upper 1 cm of sediment to background levels in 44 and 400 yr, respectively. This remobilization is a small percentage of current inputs to Narragansett Bay.

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Nous avons examiné les métaux de transition Cu, Pb, Fe, Mn et Cd, estimé les taux de mise en liberté à court et long terme depuis des sédiments fortement contaminés et comparé cette mise en liberté avec l'actuel flux de métaux dans un écosystème. La concentration de Cu et Pb augmente dans la colonne d'eau située au-dessus de sédiments marins contaminés quand ces derniers sont isolés des sources de métaux et de carbone inorganique, et maintenus dans de volumineux (13 m^3) microcosmes marins. En été et au début de l'automne, les concentrations de Cu augmentent d'un facteur 3 par rapport à la concentration dans les microcosmes contenant des sédiments légèrement pollués et non contaminés. Des calculs de bilan de masse indiquent que 840 et 21 $\mu mol \cdot m^{-2} \cdot an^{-1}$ de Cu et de Pb respectivement sont mobilisés et exportés des microcosmes contenant des sédiments fortement contaminés, tandis que les sédiments moins contaminés perdent 120 $\mu mol\ Cu \cdot m^{-2} \cdot an^{-1}$. Le fer et Mn ne sont pas exportés des microcosmes. Il est possible qu'en l'absence de taux élevés de sédimentation et de bioturbation la perte de Cu et de Pb par diffusion suffise à ramener le centimètre supérieur de sédiment aux niveaux de base en l'espace de 44 et 400 ans respectivement. Cette remobilisation ne représente qu'un faible pourcentage des apports actuels dans la baie de Narragansett.

Received March 19, 1982
Accepted November 17, 1982

Reçu le 19 mars 1982
Accepté le 17 novembre 1982

DISCHARGE of nutrients, metals, and anthropogenic organic compounds during the past century have resulted in elevated levels within Narragansett Bay, particularly in the upper region known as the Providence River (Olsen and Lee 1979). The sediments in the Providence River act as a repository for these compounds and influence the water column concentrations of nutrients (Pilson et al.1980; Nixon, Kelly et al. 1980; Nixon et al. 1976) and certain metals through both remobilization (Hunt 1983a) and depositional processes (Santschi et al. 1980a; Santschi et al. 1980b; Turekian 1977). Given the large size of the sediment reservoir and the influence of the sediments on the water column, it is not evident, a priori, if reduction in nutrient and metal loading through improved sewage treatment would result in immediate improvement in the quality of the ecosystem.

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]The contents of this article do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Printed in Canada (J6856)
Imprimé au Canada (J6856)

Several laboratory studies suggest that contaminated sediments will release metals when maintained under oxidizing conditions (Lu and Chen 1977) and also in the presence of bioturbation (W. R. Davis USEPA, Narragansett, RI, personal communication). Even though diminished pollution sources may result in decreased metal loading in natural systems (Bothner et al. 1980; Mearns 1981), the time scales for the recovery of natural systems have been estimated only for Hg (Bothner et al. 1980).

To improve our ability to predict the consequences of reducing nutrient, metal, and organic discharge into presently impacted ecosystems, we studied a gradient of contaminated sediments held under uniform low discharge conditions in controlled marine ecosystems. The study was conducted at the Marine Ecosystem Research Laboratory (MERL) from August 1979 to March 1981. The focus of this paper is on the response of several transition metals to the relaxed pollution pressure. We examined short- and long-term release of metals from highly contaminated sediments and compared these releases with estimates of present metal fluxes into Narragansett Bay.

Methods

Microcosms

For this experiment, nine microcosms each containing 13 m^3 of seawater were used. Three microcosms were used for each sediment type. The microcosms were operated with a flow through status by adding 480 L of seawater in four pulses daily (120 $L \cdot pulse^{-1}$) which gave a 27-d water turnover time. Turbulence was supplied with 2 h on, 4 h off mixing cycle from mixers located 1 m above the sediments. The microcosms were outdoors, exposed to sunlight and weather. Details of the microcosm operation have been described at length (Pilson and Nixon 1980; Nixon, Alonso et al. 1980; Pilson 1978), as has been their ability to mimic natural estuarine environments typical of the lower west passage of Narragansett Bay (Pilson et al. 1980; Hunt and Smith 1982; Oviatt et al. 1980).

Sediment

Sediments from three regions of Narragansett Bay (Fig. 1) were recovered in as natural a condition as feasible and placed within the MERL ecosystems to provide a controlled reduction in the level of organic, nutrient, and metal loading. Sediment from station II (Providence River) represents the region most strongly impacted by industrial and domestic sewage discharge and is rich in nutrients, organic material, trace metals, hydrocarbons, and other pollutants (Van Vleet and Quinn 1977, 1978; Farrington and Quinn 1973; Eisler et al. 1977). Sediment with a detectable pollutant load was collected at station I (midbay) which is the sediment source for previous MERL experiments. Clean sediments were collected from station III in Rhode Island Sound.

Experimental results which can be related to natural systems require that the sediments retain natural characteristics such as orientation, animal populations, and pore water chemistry. This was achieved by collecting sediment from each site

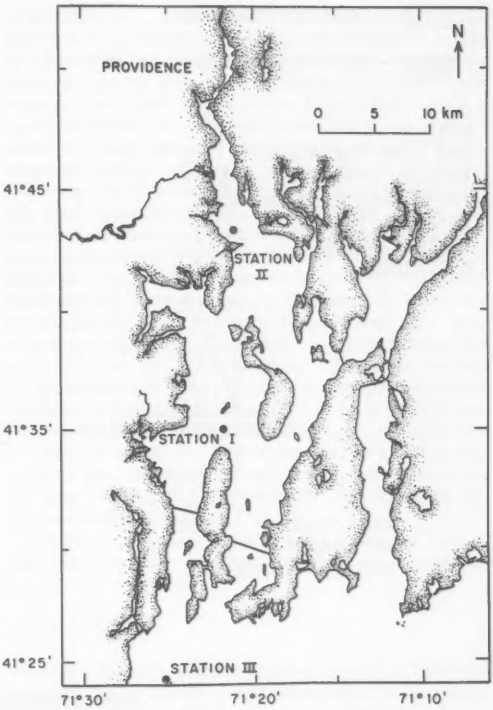

FIG. 1. Locations in Narragansett Bay (United States) from which sediments were recovered and placed in the MERL microcosms.

with a 0.25-m^2 USNEL spade corer (Fig. 2). The corer with recovered sediment was placed on a frame over a sediment tray containing core retainers constructed from steel plate. The sediment was dropped ~0.5 m into a retainer by carefully opening the corer spade. After all retainers were filled, they were lifted from the sediment tray, leaving the recovered sediment in its proper orientation and remarkably undisturbed. Sediments were covered in the field with wet bags and plywood, transported to the MERL facility, placed in the microcosms, and covered with seawater from the lower west passage of the bay. Three sediment trays from each location were recovered and placed in the microcosms between August 6 and 10, 1979. All microcosms were drained of seawater and simultaneously filled on August 11 to initiate the experiment. No abnormal changes in sediment pH or E_h resulted from the transfer operation.

Analysis

Both dissolved and particulate metal concentrations in each microcosm and feed water were determined every 2–3 wk. Particulate Fe, Mn, and Al were studied because of their involvement in metal removal processes, and both Fe and Mn respond strongly to changes in the oxidation–reduction

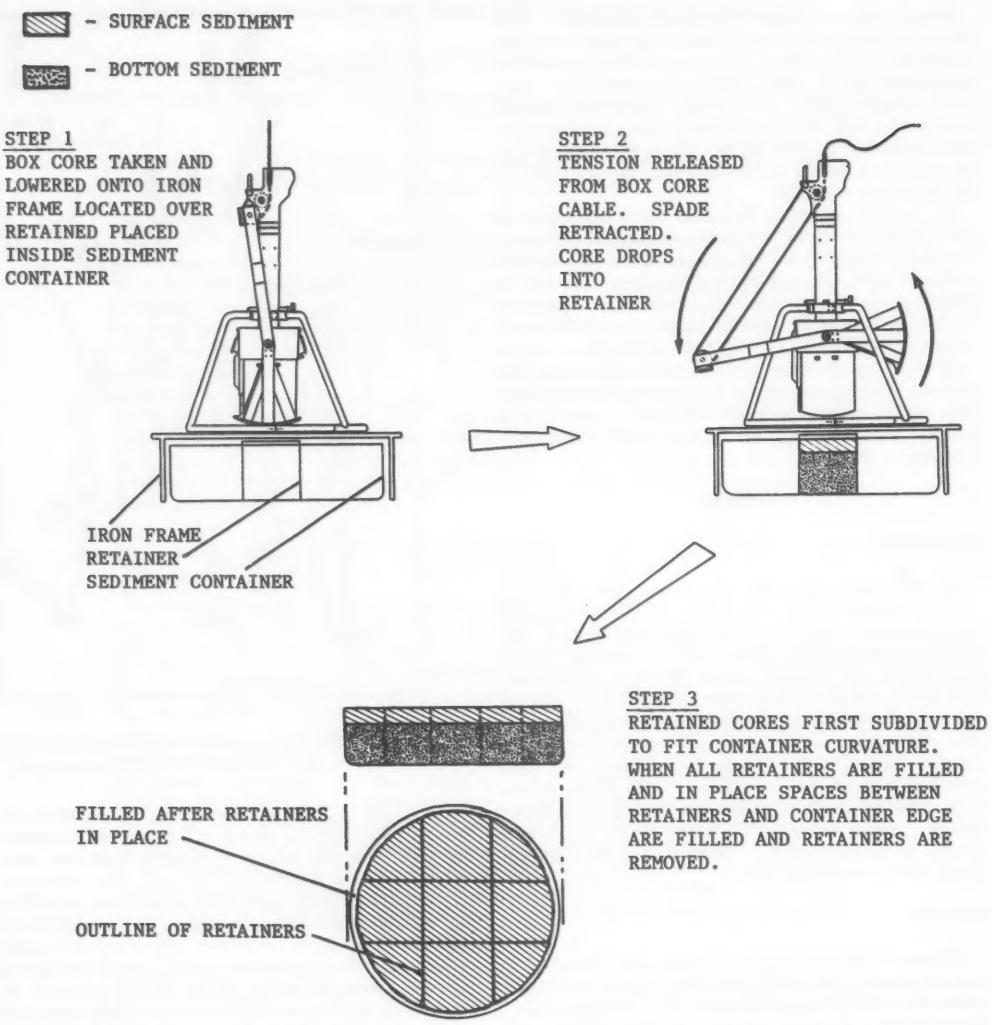
- SURFACE SEDIMENT
- BOTTOM SEDIMENT
STEP 1
BOX CORE TAKEN AND LOWERED ONTO IRON FRAME LOCATED OVER RETAINED PLACED INSIDE SEDIMENT CONTAINER
STEP 2
TENSION RELEASED FROM BOX CORE CABLE. SPADE RETRACTED. CORE DROPS INTO RETAINER
IRON FRAME
RETAINER
SEDIMENT CONTAINER
STEP 3
RETAINED CORES FIRST SUBDIVIDED TO FIT CONTAINER CURVATURE. WHEN ALL RETAINERS ARE FILLED AND IN PLACE SPACES BETWEEN RETAINERS AND CONTAINER EDGE ARE FILLED AND RETAINERS ARE REMOVED.
FILLED AFTER RETAINERS IN PLACE
OUTLINE OF RETAINERS

FIG. 2. Schematic representation of the technique developed to recover intact sediments with a 0.25-m^2 UNSEL spade corer.

potential in sediments (Aller 1980). Copper, Pb, and Cd are known pollutants affecting a variety of organisms and are major contaminants in these sediments.

Dissolved Fe, Cu, Cd, and Pb concentrations were obtained by doubly extracting ~500 mL of seawater (adjusted to pH 5) with methyl isobutyl ketone and ammoniumpyrrolidine dithiocarbamate (MIBK−APDC) after filtration through 0.4-μm Nuclepore filters. The MIBK extracts were combined and back-extracted with 5.0 mL 2 *M* HNO_3 for 48 h. Metal concentrations were determined by flameless atomic absorption spectrometry (AAS) (Perkin Elmer 603 equipped with an HGA-2100 graphite furnace and D_2 arc background correction). Standard curves for metals were made in 2 *M* HNO_3 adjusted to 550 μg $Na \cdot L^{-1}$ with metal-free seawater. Seawater was added to standard solutions to compensate for a consistent depression in analytical absorbance resulting from entrainment of sea salt in the acid extract of the MIBK−APDC phase. All extractions were completed within 4 h of sample collection. Analytical precision was within 10% of the mean, as determined from replicated samples. Intercalibration of this method with laboratories at the Graduate School of Oceanography using the Co−APDC coprecipi-

tation method gave results which agree within the analytical precision. Dissolved Mn was measured by direct injection into the graphite furnace of 0.4-μm-filtered samples after acidification (10 μL $HNO_3 \cdot mL\ seawater^{-1}$). Total Mn was obtained from unfiltered samples, acidified, and analyzed as above. Precision of the Mn analysis was <5%. Accuracy was tested by diluting NBS-1643 freshwater 1:3 with metal-free seawater and analyzing. Measured Mn (29 ± 1.5 $\mu g \cdot L^{-1}$) compared well with the certified Mn (29 ± 1 $\mu g \cdot L^{-1}$) concentration. Manganese samples were collected every 10 d.

Total suspended loads were determined from the net weight of particles retained by the 0.4-μm Nuclepore filter. Samples were washed salt free with 5 mL of high-purity water.

The particulate matter was then ashed in 1.5-cm-diameter quartz boats at room temperature to remove the filter and organic matrix, to prevent volitilization of certain metals, i.e. Cd, and to reduce the chance of contamination from reagents used in wet ashing procedures. The residue remaining from the ashing procedure was transferred to clean 7-mL scintillation vials with an Eppendorf pipet using concentrated HNO_3 (500 μL), and three 500-μL rinses with high-purity water obtained by subboiling deionized, distilled water in an all-quartz still. Concentrated HF was then added to the vial to digest siliceous material (diatoms and clay minerals). Samples were allowed to digest for at least 2 wk at room temperature prior to analysis by flame (Fe, Al, Mn) and flameless (Cu, Pb, Cd) AAS. Metal concentrations were determined against standard curves. Precision of replicated samples is within 10% of the mean. Studies using USGS-standard rock G-2 gave Al and Fe results within 10% of the certified value. Digestion blanks contribute less than 0.2, 0.06, and 0.02 $nmol \cdot L^{-1}$ Cu, Pb, Cd and less than 0.1 $nmol \cdot L^{-1}$ Mn, Fe, and Al, respectively, to the sample concentrations.

Sediment cores were collected from the sediment recovery sites in June 1979 by divers using 10-cm-diameter core liners. The cores were extruded and sliced in 1-cm sections prior to drying by lyophilization. Dry sediments were pulverized, and ~1 g was tarred into a 120-mL polyethylene digestion bottle. Fifty millilitres of 1 *M* HNO_3 was then added to the bottle, and samples were digested overnight (16 h) in a 50°C water bath. The supernatant was decanted into storage vials. Metal concentrations were determined against standard curves in 1 *M* HNO_3 by flame AAS. Low concentrations of Cd and certain other metals in the Rhode Island Sound sediments required flameless AAS for detection and quantification. Replicability is within 10% for this method.

Rates of Sediment Recovery

Calculated export or import of metals in the microcosms during the experiment was employed to estimate sediment recovery rates. Import or export in the microcosms was estimated using the equation

$$(1) \quad tf(C_T^i - C_T^o) = x$$

where t is the time interval of the experiment in days, f is the water exchange rate (480 $L \cdot d^{-1}$), C_T^i and C_T^o are the time-weighed mean total metal concentration (dissolved plus particulate) in the feed water and microcosm overflow, respectively, and x is the net amount of metal exported (−) or imported (+) to the microcosm. The rate of export or import in micromoles per square metre per day was obtained by dividing x by the area of the sediment (2.5 m^2) and time interval (days) under consideration. Recognizing that on a weekly basis there is a great deal of variability between microcosms in a single treatment group (Hunt and Smith 1982), a long-term average is a more precise measure of system responses. The short-term variability (weekly) does not usually meet statistical assumptions of normality because the processes are often exponential in nature. However, the long-term time-weighted means (in all cases examined, this is identical to the arithmetic mean) have smaller coefficients of variability and tend to be normally distributed, and thus may be statistically tested with replicate treatments. We have chosen to average over a period that is longer than the annual cycle of 12 mo, so that all fluxuations with periods less than 12 mo are included in the average. The appropriate statistical test between treatments will then contrast variability between the long-term mean within treatment groups to the difference in treatment means. We have chosen to use a two-sample *t*-test which assumes unequal within-treatment variances for the purpose of testing the statistical significance of the between-treatment variation.

Estimates of the total available metal in the top 1 cm of sediment from each treatment were calculated from the equation

$$(2) \quad R = CP\rho V$$

where R is the metal in the reservoir in moles, C is the metal concentration per unit dry weight of sediment, P is the amount of dry sediment per gram wet sediment, ρ is the wet sediment density (~1.55 $g \cdot cm^{-3}$), and V is the volume of the upper 1 cm of wet sediment in the microcosm (2.5 × 10^4 cm^3).

Results

Sediment Characteristics

The sediments from stations I and II were generally similar in grain size distribution, but station III sediments had a greater abundance of fine sands and less clay and silt (Table 1). Total organic carbon in the sediment decreases from Providence River to the Rhode Island Sound as does the percentage of water in the upper 4 cm (Table 1).

The macrofaunal community at each location was also dominated by different organisms (Table 1). During the first 4 mo the sediments were in the microcosms, the benthic macrofauna decreased by 50% in the midbay treatment and 80% in the Rhode Island Sound treatment. The Providence River treatment did not show this mortality. All treatments had similar abundances (~10 000 $animals \cdot m^{-2}$) for the remainder of the experiment (Oviatt et al. 1982). *Mulinia lateralis* was the primary benthic animal in the Providence River treatment which had very low polychaete abundance (Oviatt et al. 1982) relative to the other treatments. In the Providence River sediments the depth in the sediment at which E_h became zero decreased from 0 cm in September and October 1979 to 1.5 cm by July and October 1980 (M. E. Q. Pilson and

TABLE 1. Sediment characteristics at the three sediment recovery locations in Narragansett Bay.

	Providence River	Midbay	Rhode Island Sound
Water depth (m)	5	7	30
H_2O (%)	63	47	41
Clay (%)	36	23	18
Silt (%)	48	60	31
Sand (%)	17	18	51
Organic carbon (%)	4.5	1.6	1.0
Major macrofaunal species	*Mulinia lateralis*	*Mediomastus ambiseta*	*Nucula annulata*

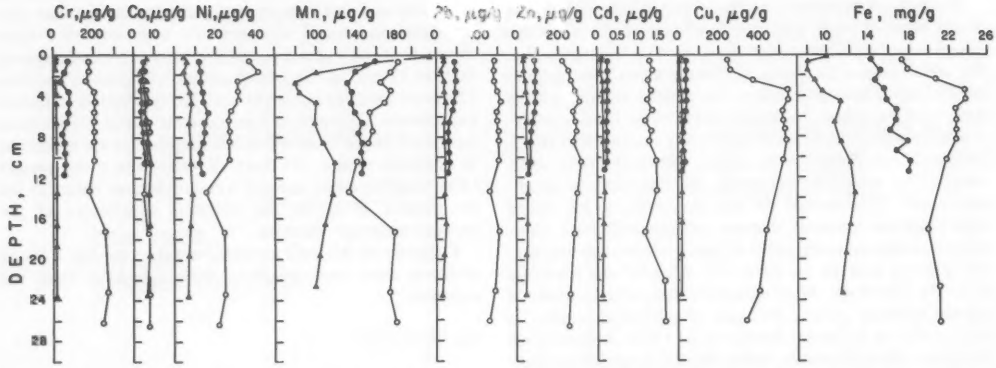

FIG. 3. Comparison of transition metal concentration in sediments from station I (midbay) (●), station II (Providence River) (○), and station III (lower bay) (▲) in Narragansett Bay.

R. Beach, University of Rhode Island, personal communication). Thus, the surface sediments of this treatment became more oxidizing, probably in response to decreased organic loading and bioturbation.

Sediment metal concentrations decrease away from the Providence River and with depth at stations I and II (Fig. 3). Station III is characterized by low and relatively constant metal concentrations. Metals in the top 1 cm of sediment were from 8 (Ni) to 28 (Cu) times higher at station II than at station I. These metals also correlate strongly with the total organic carbon present in the sediment (C. D. Hunt, unpublished data). Cobalt is not elevated at station II relative to the other stations, while Fe is 1.7 times higher. Manganese is highest in the top 1 cm of station III.

Water column metal concentrations: initial 4 mo — Transfer and containment of sediments from the three regions of Narragansett Bay did not result in massive remobilization of either dissolved or particulate metals to the water column during the first 7 d. During the 1st mo of the experiment, dissolved Mn in the Providence River treatment appeared elevated (Fig. 4), while particulate Mn was low (Fig. 5) relative to the other treatments. Total Mn remained relatively similar in all treatments (Fig. 3). Dissolved Mn in the Providence River treatment appears elevated because Mn was partitioned differently, not because of an absolute increase in Mn concentration. The difference in partitioning might have resulted because large diatom populations, which can affect the transfer of dissolved Mn to particulate Mn (Hunt and Smith 1980; Hunt 1983b), developed during the 1st mo in the Rhode Island Sound (65 000 cells·mL^{-1}) and midbay (1700 cells·mL^{-1}) treatments but not in the Providence River (60 cells·mL^{-1}) treatment.

Between August and December 1979 the mean metal concentrations in the water column of the Providence River treatment were higher than in the other treatments. Dissolved metal concentrations were generally similar in the Rhode Island Sound and midbay during this period. Dissolved Pb, Fe, and Cu were as much as a factor of 2 higher in the Providence River treatment relative to the Rhode Island Sound treatments (Fig. 4). During this same period, particulate Cu increased by at least a factor of 2 in the Providence River treatment (Fig. 5). Particulate Cd and Pb were not different between treatments. The highest particulate Fe and Al concentrations were present in the midbay treatments initially but decreased to concentrations consistent with the other treatments by December. All treatments had relatively similar dissolved and particulate metal concentrations during the winter of 1980.

Water column metal concentrations: long term — The long-term response of the particulate and dissolved metals can

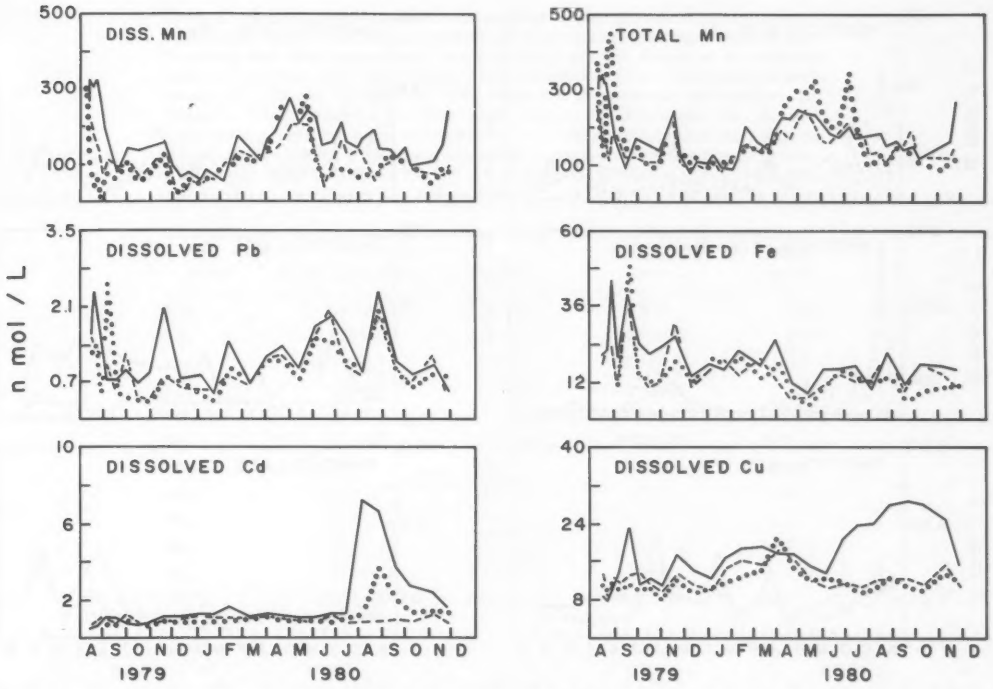

FIG. 4. Mean dissolved metal concentration measured in the water column of each treatment during the sediment recovery experiment. Each treatment represents the mean of three microcosms per treatment per sample period. —, Providence River; ---, Midwest Passage; ···, Rhode Island Sound.

be separated into those having a seasonal response and those without. Dissolved and particulate Cd and particulate Al were the only metals not undergoing seasonal changes in any treatment (Fig. 3 and 4). Particulate Cu did not change seasonally in the midbay and Rhode Island Sound treatments but did show a minimum in the Providence River treatment in January and February. Dissolved Cu increased in all treatments during the spring and then decreased. In the Providence River treatment, dissolved Cu increased again in early June. This increase continued until the following November. Each Providence River microcosm had slightly different time trends but generally reached the highest concentrations observed in the early fall of 1980 (Fig. 6). The maximum dissolved Cu observed in each of these microcosms was 3–4 times those observed in the Rhode Island Sound microcosms over the same time period.

Dissolved Fe was slightly lower during the summer and fall than during winter and spring. A minimum in particulate Fe occurred during the summer in both the Rhode Island Sound and midbay treatments but not in the Providence River set. Particulate Pb was also low in the summer and fall when dissolved Pb reached maximum values.

Manganese showed a strong spring maximum, similar to that observed in previous experiments in these ecosystems (Hunt and Smith 1982). However, particulate Mn was constant throughout the experiment except during the summer in the Rhode Island Sound and midbay treatments which showed elevated concentrations.

The long-term treatment means were the same for all metals in the Rhode Island Sound and midbay treatments except for particulate Mn (Table 2). Several parameters in the Providence River treatment including particulate Fe, Al, and Cd, suspended load, and dissolved Cd were also similar to the other treatments. The remaining metals were generally elevated in the water column overlying the highly contaminated Providence River sediments relative to the other treatments (Table 2). The mean dissolved Cu concentration in the three Providence River microcosms was 30–40% higher and particulate Cu was 2–3 times that in the other treatments. Elevated dissolved Fe was found in only one microcosm. Dissolved Pb was slightly higher in the Providence River treatment but particulate Pb became elevated only in the late summer and fall of 1980. Manganese in this treatment was high in the dissolved phase but low in the particulate phase relative to the other treatments.

Differences in the mean metal concentrations in the feed water and microcosms were also evident (Table 2). Generally, the feed water had higher concentrations of particulate Fe, Pb,

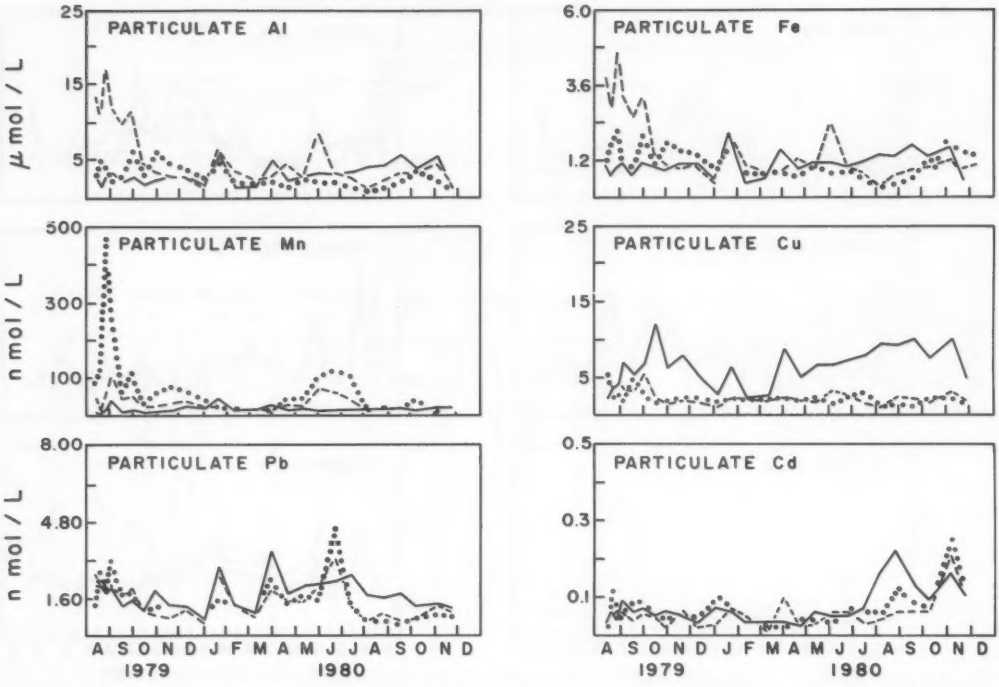

FIG. 5. Mean particulate metal concentrations measured in the water column of each treatment during the sediment recovery experiment. Each treatment is the mean of three microcosms per treatment per sample period. —, Providence River; ---, Midwest Passage; ···, Rhode Island Sound.

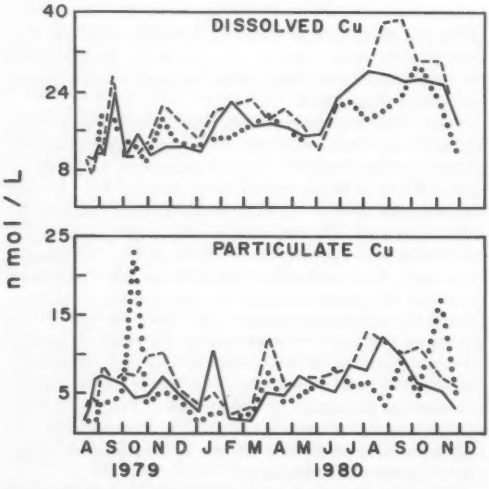

FIG. 6. Response of dissolved and particulate Cu to relaxed metal and organic loading in three microcosms containing polluted sediments. —, microcosm 2; ---, microcosm 7; ···, microcosm 9.

Cd, and Al, suspended load, and dissolved Cd but lower dissolved Cu and Pb than the microcosms (Table 2). Dissolved Fe in the feed water was not different from that in the microcosms, while differences in particulate Cu and Mn and dissolved Mn varied with treatment.

METAL EXPORT OR IMPORT RATES

Export or import of several metals from individual microcosms was evident from the difference between the long-term mean concentrations in the feed water and those in the microcosms. Copper and Cd were exported from all microcosms under the experimental conditions (Table 3). Lead was exported from the Providence River treatment but was imported to the other treatments. Iron and Mn were imported to all microcosms.

The elevated Cu concentrations in the water column of the Providence River treatment apparently resulted from a flux of Cu from the sediments. Conceivably, the rate at which Cu was removed from the water column may have slowed with resultant increases of Cu in the water column. This is unlikely, since Cu is a particle reactive element having half-removal times in the order of 5–10 d during the summer (C. D. Hunt, unpublished data).

Both the temporal response for Cu and the long-term mean

TABLE 2. Mean dissolved (subscript d) and particulate (subscript p) metal concentrations in the water column overlying sediments with three different pollution loadings, August 1979 to November 1980. Metal concentrations are in nanomoles per litre. Results are the treatment mean ± 1 SD based on the time-weighted mean concentration in each microcosm between August 13, 1979, and November 24, 1980. Means that are statistically different from the Providence River treatment at $P < 0.05$ (single rule) and $P < 0.10$ (double rule) are indicated. All other treatments are not different at $P < 0.10$ except particulate and total (subscript t) Mn between the Rhode Island Sound and midbay treatments. (Conversion factors: 10 nmol $Cu \cdot L^{-1}$ = 0.63 $\mu g \cdot L^{-1}$; 1 nmol $Cd \cdot L^{-1}$ = 0.11 $\mu g \cdot L^{-1}$; 1 nmol $Pb \cdot L^{-1}$ = 0.21 $\mu g \cdot L^{-1}$; 10 nmol $Fe \cdot L^{-1}$ = 0.56 $\mu g \cdot L^{-1}$; 100 nmol $Mn \cdot L^{-1}$ = 5.5 $\mu g \cdot L^{-1}$; 100 nmol $Al \cdot L^{-1}$ = 2.7 $\mu g \cdot L^{-1}$.)

Metal[a]	Rhode Island Sound	Midbay	Providence River	Feed water
Cd_d	0.9±0.1[b]	0.96±0.02	1.2[c]	0.60
Cd_p	0.07±0.01	0.06±0.02	0.08±0.01	0.10
Cu_d	12.1±0.4	12.9±0.4	18.9±2.0	9.6
Cu_p	2.2±0.5	2.3±0.5	6.6±0.9	3.9
Fe_d	14±1	15±1	19±3	15.6
Fe_p	980±100	1300±400	1080±140	1900
Mn_d	100±6	110±17	150±7	156
Mn_p	62±13	33±16	15±2	48
Mn_t	167±10	150±7	165±5	212
Pb_d	0.91±0.12	0.95±0.03	1.17±0.02	0.79
Pb_p	1.44±0.11	1.33±0.15	1.70±0.2	1.78
Al_p	2700±400	4500±1500	3200±400	6600
Total suspended load ($mg \cdot L^{-1}$)	2.5±0.1	2.8±0.8	2.6±0.2	3.7

[a]Subscript d, dissolved; subscript p, particulate; subscript t, total.
[b]Excludes results from microcosm 4.
[c]Result for microcosm 7 only.

concentration were used to estimate the net rate at which Cu was supplied to the water column by the Providence River sediments. Since each microcosm responded differently in detail (Fig. 6), the rate for the treatment was not determined until estimates for individual microcosms were made. In microcosm 2, constant total concentrations between August and November required a flux of 0.19 $\mu mol\ Cu \cdot m^{-2} \cdot h^{-1}$. Copper concentrations in microcosms 7 and 9 did not remain constant for sustained periods. Therefore, import−export calculations for each sample period were used to estimate that 0.08−0.36 $\mu mol\ Cu \cdot m^{-2} \cdot h^{-1}$ was necessary to produce the observed changes in Cu concentrations. The average flux in microcosms 7 and 9 from June to November was 0.24 ± 0.06 and 0.16 ± 0.07 $\mu mol\ Cu \cdot m^{-2} \cdot h^{-1}$, respectively. Combining estimates of the Cu flux results in an estimated treatment flux of 0.2 ± 0.07 $\mu mol\ Cu \cdot m^{-2} \cdot h^{-1}$ (4.8 ± 1.7 $\mu mol\ Cu \cdot m^{-2} \cdot d^{-1}$) during the summer and fall of 1980. This compares with an annual flux of 2.3 $\mu mol\ Cu \cdot m^{-2} \cdot d^{-1}$ using the long-term concentration (Table 3). The source of the Cu is assumed to be the contaminated sediments and represents the net flux from the sediment under these experimental conditions.

Export of Cu during the summer was 60% of the total exported during the 16 mo that Cu was measured in the experiment. Export of Cu during the summer−fall period represents 75% of the annual loss of Cu from the microcosms. Thus, Cu was lost about 3 times faster during the warm months of the second summer than during the winter months. The other treatments also exported Cu but at lower rates than the Providence River treatment.

The estimated loss of Cu from the sediment of the Providence River microcosms is not within the precision of analytical measurement of metals in sediment (10%) being 3−5% of the total reservoir (Table 4). Thus, a very small depletion of Cu in the surface sediment resulted in sizeable elevation in the dissolved and total Cu in the water column. Assuming zero-order kinetics and negligible sedimentation rates, the time required to purge the top 10 cm of the Providence River and midbay sediments of their Cu burden would be ~400 yr if all pollutant pressure were curtailed and conditions in the field were similar to the microcosms.

Lead was exported from the Providence River treatment only (Table 3). The export rate was slow and was sufficient to deplete the Pb sediment reservoir by 0.4%. At this rate, ~3200 yr would be required to cleanse the top 10 cm of these sediments using the same assumptions as above. The net import of Pb (also Fe and Mn) to the other treatments suggests that retention of these metals was occurring. The fact that all

TABLE 3. Estimates of the total metal export or import in the sediment gradient experiment between August 1979 and November 1980. Export or import is compared with the metal reservoir in the upper 1 cm of the sediment column from each sediment type.

Metal	Treatment	Total export−import[a] ($\mu mol \cdot experiment^{-1}$)	Export−import rate ($\mu mol \cdot m^{-2} \cdot d^{-1}$)	Sediment reservoir[b] ($mol \cdot microcosm^{-1}$)	% reservoir exported−imported
Cu	Providence River	-2.7×10^{-3}	−2.3	0.092	−2.9
	Midbay	-0.38×10^{-3}	−0.33	0.014	−2.7
	Rhode Island Sound	-0.19×10^{-3}	−0.16	0.0033	−5.8
Fe	Providence River	+0.21	+180	7.3	+2.9
	Midbay	+0.14	+0.20	6.1	+2.3
	Rhode Island Sound	+0.18	+160	4.1	+4.4
Pb	Providence River	-67×10^{-6}	−0.058	0.017	−0.4
	Midbay	$+65\times10^{-6}$	+0.056	0.0047	+1.4
	Rhode Island Sound	$+49\times10^{-6}$	+0.042	0.0016	+3.1
Mn	Providence River	$+9.4\times10^{-3}$	+8.1	0.083	+11.3
	Midbay	$+13.7\times10^{-3}$	+11.7	0.056	+24.5
	Rhode Island Sound	$+8.8\times10^{-3}$	+7.5	0.061	+14.4
Cd	Providence River (No. 7)	-0.13×10^{-3}	−0.11	0.27×10^{-3}	−48
	Midbay	-0.072×10^{-3}	−0.06	0.052×10^{-3}	−138
	Rhode Island Sound (Nos. 3 and 6)	-0.061×10^{-3}	−0.05	0.018×10^{-3}	−2.9

[a]−, export from microcosm; +, import to microcosms.
[b]Reservoir shown is for the top 1 cm of the sediment.

TABLE 4. Comparison of the daily input of Cu, Pb, and Cd to Narragansett Bay with the potential input from remobilization from contaminated sediment from the Providence River and upper Narragansett Bay.

Metal	Input to bay[a] ($mol \cdot d^{-1}$)	Remobilized from sediment: Providence River[b] ($mol \cdot d^{-1}$)	Remobilized from sediment: Upper bay[c] ($mol \cdot d^{-1}$)
Cd	48	2	5
Cu	3000	46	100
Pb	780	1	2.5

[a]Estimated additions from all sources from Olsen and Lee (1979) and C. D. Hunt (unpublished data).
[b]Area 20.07 km^2.
[c]Area 44.67 km^2 including the Providence River.

systems receive the same input water and that Pb was exported from the Providence River treatment further supports an active remobilization of Pb from these sediments. Cadmium was apparently exported from all treatments (Table 3). However, the problems with the large nonspecific inputs of Cd to some of the microcosms in the fall of 1980 precludes a rigorous examination of the export rate. The results suggest that all sediment types may have lost Cd and that the loss rate from the Providence River treatment may have been higher than in the other treatments.

Discussion

The intent of the sediment gradient experiment was to establish temporal changes in stable metal concentrations in the water column in response to relaxed pollution pressure and to estimate long-term release rates from the sediment. The experiment has shown that metals have distinct responses both temporally and in response to the sediment type. Elevated concentrations of Cu, Cd, and Pb were observed in the water column overlying the highly polluted Providence River sediments. Mass balance considerations and the time trend analysis demonstrate there is a tendency for polluted sediments to purge themselves when pollution pressure is reduced. The onset of the purging process was not immediate, requiring at least one seasonal cycle before large shifts in the water column metal were apparent. In natural systems, the purging process may operate but is overwhelmed by the magnitude of pollutant inputs so that it is not detectable under field conditions (Table 4). If the remobilization rates observed in this experiment are applicable to the Providence River system, <5% of the metal entering the water column would be from the sediments. The slow sediment recovery rates observed in this experiment suggest that metal contaminants currently in sediments will remain for many years.

It is also important to address causes for the observed remobilization of these metals. Physiochemical factors

TABLE 5. Reduction in productivity and organic loading in Providence River microcosms relative to field conditions.

Region	Net daylight production ($g\ C \cdot m^{-2} \cdot yr^{-1}$)	BOD_5 loading[b] ($g\ C \cdot m^{-2} \cdot yr^{-1}$)
Providence River, 1971–73	429[a]	116
Narragansett Bay (west passage)	277[a]	—
MERL		
Control microcosms		
1978–79	276[a]	
1979–81	200[c]	
Providence River		
1979–81	322[c]	
April 1980–81	207	
Rhode Island Sound		
1979–81	238[c]	

[a]From Oviatt et al. (1981).
[b]Calculated from Robadue et al. (1981) using the net BOD_5 input to the Providence River, a respitory quotient of 1.0, and a C/O_2 ratio of 0.375.
[c]Total system production converted from weekly diurnal O_2 changes (Oviatt et al. 1982).

affecting remobilization of certain metals from contaminated sediments include salinity, pH, and the oxidation–reduction condition of the sediment (Gambrell et al. 1980). In the present experiment, relocation of polluted sediment resulted in two distinct changes: (1) the sediment was isolated from metal sources and (2) organic loading factors were reduced by ~60% (Table 5). The reduction in organic load included both primary production, particularly during the summer of 1980, and inputs from sewage treatment plant effluents (Table 5).

Input of organic carbon to sediments is a fundamental driving force in creating and maintaining reducing conditions in sediments (Berner 1980). This organic matter has been suggested as a major factor maintaining metals in estuarine sediments (Hunt 1979, 1981). Oxidation of the organic matter may lead to release of metals as redox potential, organic content (Lu and Chen 1977), and sulfide concentrations (Boulegue et al. 1982) adjust. Such release of Cd, Zn, Ni, Cu, and Cr but not Fe and Mn has been observed when polychaetes were added to polluted organic-rich reducing sediments, and the resulting burrow walls, which become oxidizing, were examined for changes in metal content (W. Davis, USEPA, Narragansett, RI, personal communication). We suggest that the elevated Cu and Pb concentrations in the water column over the Providence River sediment occurred because the organic input was reduced allowing the sediments to become oxic with concomitant release of these metals. Bioturbation by benthic animals may also have accelerated this process. Although the relative importance of this effect could not be determined from the available data, burrowing worms were less abundant by a factor of 10–20 in the Providence River treatment than in the other treatments, suggesting this process was less important.

Extension of the results of this experiment to natural systems must be made with caution, as many other factors operate within natural estuaries which may alter the rate of sediment recovery, including (1) assumptions that metal loading factors will decrease, (2) effects of different flushing rates, (3) transport of metal away from contaminated areas by normal estuarine processes and circulation, (4) effects of depositional processes on removing remobilized metals back to sediments, (5) the rate at which new sediment is deposited and contaminated sediment is buried, and (6) effects of bioturbation on metal mobilization.

This experiment suggests that the quality of sediment can influence the water column metal concentrations. Thus, sediments not only act as a sink for many metals but under appropriate conditions may function as a source of metals to the water column. This is of concern in those situations when contaminated sediment comes in contact with unpolluted water, since Cu has detrimental effects on plankton (Thomas et al. 1980; Hollibaugh et al. 1980). In those ecosystems which do not have sufficient capacity to complex Cu remobilizing from a contaminated sediment, greater negative effects may be experienced than in systems with high complexing capacity, i.e. oceanic water versus coastal or estuarine regions, since a greater fraction of the Cu may be in the Cu^{2+} form, the most toxic Cu species (Sunda and Guillard 1976; Sunda and Gillespie 1979; Gavis et al. 1981). Thus, selection of sites to receive wastes should be undertaken with full recognition of the potential long-term bleed of toxic elements from the sediments. The results further suggest that selection of depositories for polluted sediment or other waste material should consider the organic loading to the sediments, i.e. productivity in the water column, so as to minimize the remobilization of these contaminants to the water column.

Acknowledgments

Eric Klos developed and supervised the sediment recovery operation. Sediment analyses were performed by J. Hopkins. C. Oviatt, P. Donaghay, P. Santschi, and an unidentified reviewer offered helpful criticism of the original manuscript. The project was funded by Environmental Protection Agency grants CR807795 and 806072020.

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The Behavior of Arsenic in Selected United Kingdom Estuaries[1]

W. J. LANGSTON

Marine Biological Association of the United Kingdom, Citadel Hill, Plymouth PL1 2PB, England

LANGSTON, W. J. 1983. The behavior of arsenic in selected United Kingdom estuaries. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 143–150.

High As concentrations occur in certain United Kingdom estuaries as a result of mineralization and associated processes including mining and metal refining. Analyses of dissolved and particulate As, carried out in estuaries of differing contamination, indicate that As is readily precipitated with Fe during mixing at the freshwater–seawater interface. This gives rise to significant correlations between the two elements in suspended and bottom sediments. More than 80% of the As entering Restronguet Creek, the most contaminated of the estuaries studied, is retained by estuarine sediments, which consequently act as sinks for riverine inputs and limit transport of dissolved species to coastal waters. However, the behavior of As in different estuaries varies with the physicochemical conditions present and the nature of the source. Most significantly, remobilization of sediments is recognized as a feature affecting the cycling of As in the Tamar Estuary.

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On trouve dans certains estuaires du Royaume-Uni des concentrations d'As élevées résultant de la minéralisation et des processus qui lui sont associés, y compris l'extraction et le raffinage du métal. On constate, après analyses de l'As dissous et particulaire effectuées dans des estuaires diversement contaminés, que l'As précipite facilement avec le Fe au moment du mélange à la surface de contact eau douce-eau salée. Il en résulte des corrélations significatives entre les deux éléments dans les sédiments en suspension et ceux du fond. Plus de 80 % de l'As pénétrant dans le ruisseau Restronguet, le plus contaminé des estuaires étudiés, est retenu par les sédiments estuariens, qui agissent donc comme réservoirs d'apports fluviaux et limitent le transport de l'élément dissous dans les eaux côtières. Cependant, le comportement de l'As dans différents estuaires varie selon les conditions physico-chimiques présentes et la nature de la source. On se rend compte, ce qui est très important, que la remobilisation des sédiments est une caractéristique qui influe sur le recyclage de l'As dans l'estuaire de la Tamar.

Received March 19, 1982
Accepted November 8, 1982

Reçu le 19 mars 1982
Accepté le 8 novembre 1982

ARSENIC is one of the most toxic and, because of its solubility, most available of all metals (Wood 1974). Arsenite inhibits thiol-dependent enzymes and, being of greater persistence, is considered more toxic than arsenate, which may be excreted rapidly by organisms. Nevertheless, arsenate can inhibit ATP formation by uncoupling oxidative phosphorylation. More recently, organoarsenic compounds have been used as replacements for inorganics in pesticide formulations.

The most common species in natural waters are arsenite and the more thermodynamically favored arsenate (Andreae 1978, 1979; Klumpp and Peterson 1979). Evidence suggests some biological mediation of As speciation in the oceans. Thus, arsenate may be taken up in competition with chemically similar phosphate (Sanders and Windom 1980), resulting in the release of arsenite and organoarsenic compounds into the sea (Johnson and Burke 1978; Andreae and Klumpp 1979).

As is introduced into aquatic systems naturally by geological weathering and geothermal activity or from a variety of industrial and domestic sources including mining and processing of ores, burning of fossil fuels, manufacture of chemicals, agriculture, and urban waste disposal. Estuaries are frequently exploited as dispersal media for such discharges and are an important pathway for elements such as As between their source, either natural or anthropogenic, and coastal waters. Understanding the processes of mixing, precipitation, and loss of potential contaminants to sediments together with remobilization by chemical, physical, or biological mechanisms in the estuarine zone is therefore vital in the assessment of pollution problems in areas such as the North Atlantic. It is the purpose of the present paper to report on the reactivity and transport of As in United Kingdom estuaries, in particular those of mineralized southwest England, and to

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6857)
Imprimé au Canada (J6857)

FIG. 1. England and Wales showing positions of estuaries sampled. 1, Restronguet Creek; 2, Tamar; 3, Avon; 4, Humber.

compare these data with studies of As behavior in United States estuarine and coastal areas.

Materials and Methods

COLLECTION OF SAMPLES

Restronguet Creek and the estuaries of the Tamar and Avon rivers are situated in the southwest of England (Fig. 1) and drain areas of different degrees of mineralization. The main source of contamination into Restronguet Creek is the Carnon River which cuts through highly metalliferous Devonian rocks. This river also receives adit drainage from Wheal Jane and Mount Wellington mines in addition to a number of previous workings, and high levels of As, Cu, Fe, Pb, Sn, and Zn have been reported (Hosking and Obial 1966; Bryan 1980). Restronguet Creek extends for some 4 km before draining into the Carrick roads at the seaward end of the Fal Estuary complex.

The catchment area of the Tamar has long been associated with the mining and smelting of metal ores and was at one time the scene of half the world's As production. Although the majority of this activity ceased at the end of the last century, drainage from sulphide lodes, adit portals, and spoil heaps still contributes to elevated metal levels in waters and sediments (Aston et al. 1975). Samples were taken between the mouth of the Tamar and a weir 32 km upstream. The estuarine region is more extensive than Restronguet Creek or the Avon and the salt wedge may penetrate varying distances depending on conditions of flow, usually between 21 and 26 km from the mouth.

The Avon lies east of the major metalliferous lodes in southwest England and, in contrast with the other estuaries, has no connections with mining. The estuary, approximately 7 km in length, receives drainage predominantly from moorland and agricultural land, with no major industrial inputs.

Midriver water samples were taken from a boat along the length of each estuary during a 2-h period around high water. A length of PVC tubing placed just below the surface was used to siphon water into glass flasks using a hand vacuum pump. Following removal of an aliquot for salinity determination all samples were quantitatively filtered through preweighed 0.45-μm Millipore filters into acid-washed, deionized water rinsed glass flasks. The filters were subsequently air-dried and reweighed to determine suspended particulate matter, and the sediment was extracted with distilled 1 *M* HCl for 2 h at room temperature to determine the proportion of surface-bound particulate metal. Water samples were returned to the laboratory and As^{3+} measured within 24 h. During this period no significant oxidation to As^{5+} occurs. After removal of aliquots for As^{3+} determination, water samples were acidified with distilled HCl and subsequently analyzed for total dissolved As and various metals.

A limited number of unfiltered samples were collected from the Humber Estuary. This is an area of specific interest in studying the comparative behavior of As, due to the presence of a metal refinery which discharges low pH, metal-rich effluents into the estuary.

ANALYSES

Determinations of As species in water samples were based on a pH-selective reduction to hydride by sodium tetrahydroborate and subsequent determination of cryogenically trapped arsine by flameless atomic absorption spectrophotometry.

Fifty millilitres of the unacidified sample, buffered at pH 4 with 2 mL of 5% potassium hydrogen phthalate, was treated with 5 mL of 1% sodium tetrahydroborate solution (Ventron) using a modified Perkin Elmer MHS-20 hydride system. At this pH only trivalent As was reduced to arsine, which was collected in a liquid nitrogen trap consisting of a glass U-tube (4 mm inside diameter) loosely packed with glass wool. The reaction was allowed to continue for 2 min before the trap was removed from the liquid nitrogen and the collected arsines subsequently volatilized at air temperature. A stream of nitrogen gas (100 mL/min) transported the arsines to an electrothermally heated quartz furnace (900°C) mounted in a Perkin Elmer 306 atomic absorption spectrophotometer equipped with an As electrodeless discharge lamp. Absorbances were measured as peak heights on a chart recorder and quantified by comparison with peak heights of standard solutions treated identically.

Separate subsamples were analyzed for total dissolved As (arsenate + arsenite) by acidifying 9 mL of the sample with 1 mL of 50% HCl and reacting with 5 mL of 5% sodium tetrahydroborate, using the same apparatus. Arsine, generated by both inorganic species at this pH (0.5–1.0), was trapped for 40 s before volatilization and detection. Arsenate concen-

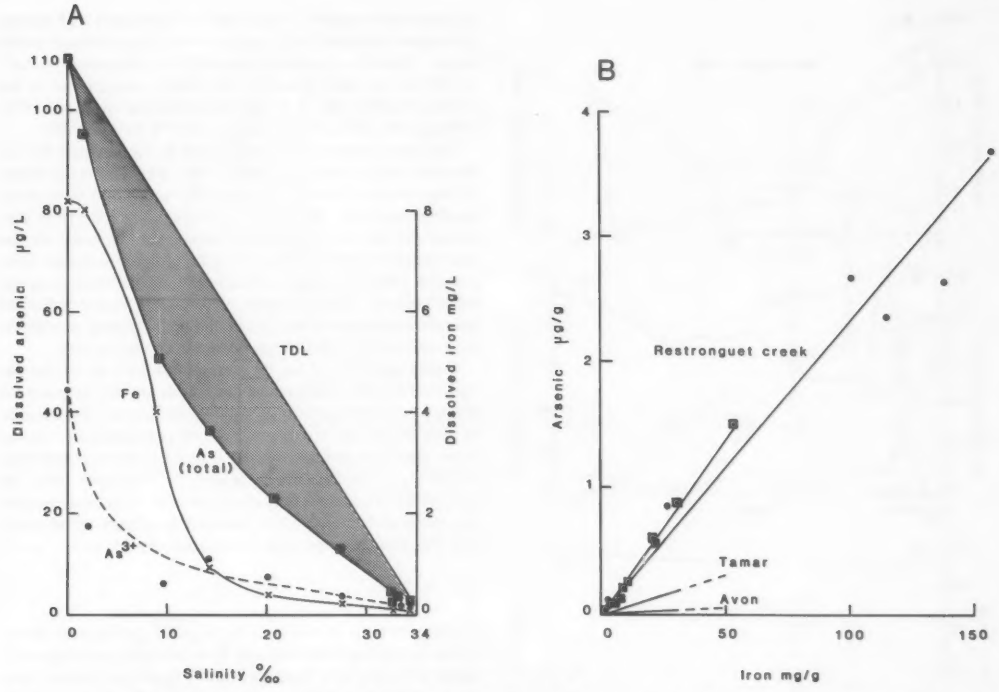

FIG. 2. (A) Distribution of dissolved metals in Restronguet Creek. The shaded area under the theoretical dilution line (TDL) indicates removal of As from solution. (B) Relationships between As and Fe in suspended particles (●) and bottom sediments (■) from Restronguet Creek. The regression plots for Tamar and Avon suspended particles are also included. Regression equations for Restronguet suspended, bottom, Tamar suspended, and Avon suspended particulates, respectively, are As (µg/g) = 19.74Fe (mg/g) + 19.75 (n = 10, r^2 = 0.9301); As (µg/g) = 31.26Fe (mg/g) − 105.7 (n = 8, r^2 = 0.9948); As (µg/g) = 6.88Fe (mg/g) − 16.6 (n = 15, r^2 = 0.9710); As (µg/g) = 1.292Fe (mg/g) + 2.8333 (n = 12, r^2 = 0.9756).

trations can thus be determined by subtracting arsenite values from the total dissolved As concentrations.

The detection limits, using the criterion of twice the standard deviation of six blank determinations, were 0.96 and 0.97 ng for As^{3+} and total dissolved As, respectively (0.02 µg/L when 50-mL samples used). Analyses of deionized water samples subjected to the complete collection procedure were not significantly different from reagent blanks (0.028 µg/L). Details of precision, recoveries, and verification of the analytical method, together with sediment collection and measurement, are described elsewhere (Langston 1980).

Water samples were analyzed for iron colorimetrically using a bathophenanthroline method (Strickland and Parsons 1968) or by graphite furnace atomic absorption spectrometry (Sturgeon et al. 1979). Similar results were obtained using both methods.

Results

RESTRONGUET CREEK

The behavior of dissolved As and Fe in Restronguet Creek during mixing of fresh and saline waters demonstrates significant reactivity rather than simple physical mixing of the two end members (Fig. 2A). High dissolved As concentrations occurred in freshwater entering the creek, ranging from 33 to 209 µg/L, due to the influx of acidic wastes from past and present mining activities. Values of pH ≤ 4 were often encountered in the Carnon River which resulted in enhanced levels of other metals associated with regional sulphide lodes including Fe (8.6 mg/L), Cu (0.5 mg/L), Zn (57 mg/L), and Mn (3.3 mg/L).

Extensive removal of "soluble" Fe was observed at low salinities in the estuary due to precipitation/coagulation mechanisms. Moving seawards, less than 10% of the Fe present in freshwater remained in solution at 50% dilution (18‰) with seawater. A corresponding deviation from theoretical dilution was observed for dissolved As (Fig. 2A). Less than 25% of the As present in freshwater remained in solution at a salinity of 18‰.

Similar results were obtained in the laboratory by mixing freshly collected filtered river water with differing amounts of filtered seawater, indicating that resulting freshly formed Fe

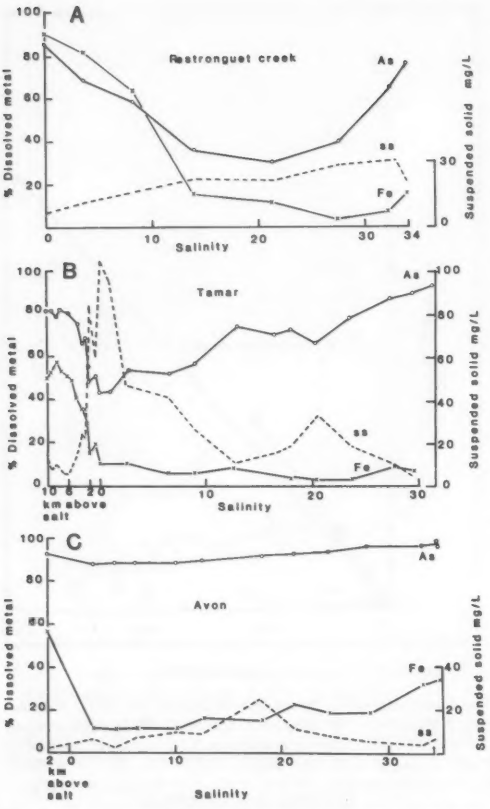

FIG. 3. Proportions of dissolved metals and suspended solids along (A) Restronguet Creek, (B) Tamar Estuary, and (C) Avon Estuary.

particles scavenge As from solution by coprecipitation at low salinities. More direct evidence of coprecipitation of As with Fe is implied by the highly significant correlations between these two metals in suspended particles ($r^2 = 0.9301$) and bottom sediments ($r^2 = 0.9948$) (Fig. 2B). There is no significant difference between metal ratios in either type of particle, suggesting that levels of As and Fe in the water column provide a significant contribution to bottom surface sediments. Resuspension of bottom material is unlikely to be significant in the stratified, low tidal energy conditions normally encountered in these waters.

The proportions of the different forms of As change according to conditions of flow and time of year but the results shown in Fig. 2A and 3A are typical examples of the behavior of As species in Restronguet Creek. The proportion of As^{3+} in acidic freshwater decreases from 40 to 10% under the rapidly changing redox and pH conditions in the upper estuary. Whether this is due to the oxidation of As^{3+} to As^{5+} or the more rapid removal from solution of the former species is not clear. However, oxidation of As^{3+} to As^{5+} is thought to proceed more rapidly in acid solutions compared with neutral pH values (Kolthoff 1921) and may be of significance in this region. There is a gradual increase in the proportion of As^{3+} to 20% of the total dissolved As at the seaward end of the estuary possibly due to biological mediation (Andreae 1978; Johnson and Burke 1978; Sanders and Windom 1980).

The percentage of dissolved As and Fe may exceed 80% of the total metal entering the creek (Fig. 3A). This value drops during mixing as levels of suspended solids and their metal burdens increase. At the mouth of the creek, levels of dissolved As are similar to background levels reported for the open ocean (Andreae 1978), and the proportion in this form is again, unlike Fe, approximately 80% of the total As in the water column. Clearly, much of the As input has remained bound to sediments in the creek, and under normal conditions little As (or Fe) will be transported to coastal waters.

Calculations based on the assumption that all of the incoming Fe is deposited in the creek indicate that between 80 and 100% of the waterborne As must be retained by particles to account for the observed sediment concentrations. Using mean flow data and an average total As water concentration of 233 μg/L for the period January 1978 to April 1981, an estimated 9.3 t of As is deposited annually in creek sediments as a result of mine drainage. Availability of particulate metal will therefore be important to estuarine organisms.

TAMAR

Interpretations of the profile of metal distribution in the Tamar Estuary is made difficult by a complex combination of inputs including adit drainage, runoff from spoil heaps, pore water influxes, and a variety of industrial and domestic sources. In addition, cyclic variability of tidal amplitude and associated phenomena such as turbidity maxima, together with a more random variability in freshwater composition, make identification of only the more obvious processes possible. An intensified study is in progress aimed at producing a more quantitative assessment of As profiles.

Dissolved As increases sharply in the freshwater region (Fig. 4A) as the river flows through a mineralized area littered with old mines and their associated adits and spoil heaps. However, the maximum As concentrations were an order of magnitude less than Restronguet Creek levels, and pH values were always between 7 and 8. Removal of a significant amount of dissolved As (30%) together with most of the "dissolved" Fe was a prevalent feature at low salinities. Subsequently, an extended midestuarine maximum is observed for As but not for Fe. Such broad maxima may be the result of injections from metal-enriched pore waters from the large areas of intertidal mudflats (Morris et al. 1978; Knox et al. 1981). The discovery of elevated levels of As (15–22 μg/L) in interstitial water samples collected along the length of the estuary is consistent with this hypothesis.

In contrast, the behavior of As^{3+} (30% of total dissolved As in freshwater, decreasing to 3% at low salinities and increasing to 12% at high salinities) appeared to be more conservative in the estuary than the predominant As^{5+} species. The sharp As^{3+} maximum (1 μg/L) observed in the freshwater zone is consistent with a localized input (Knox et al. 1981), and high values for As^{3+} (~50 μg/L) have been measured in

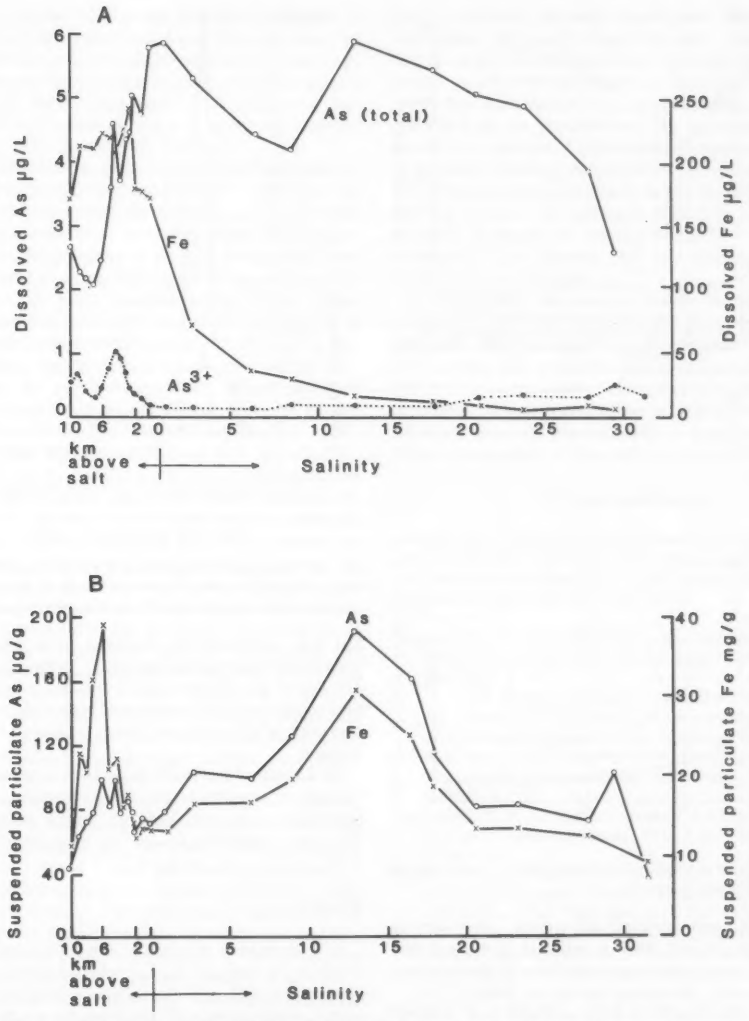

FIG. 4. Distribution of (A) dissolved metals and (B) particulate As and Fe in the Tamar and its estuary.

adit samples in this region.

Extremely good correlations between particulate As and Fe were obtained for suspended and bottom estuarine sediments ($r^2 = 0.9627$ and 0.9182, respectively). The results for suspended particles (Fig. 2B and 4B) provide evidence for increasing coprecipitation of As and Fe at salinities between 0 and 15‰, where removal from solution has been shown to occur. Although particulate As and Fe concentrations correlated well ($r^2 = 0.8912$) in the freshwater zone, ratios of As:Fe changed sharply at the interface and were much lower than in the estuarine region.

The proportions of dissolved:total As and Fe declined downstream to a minimum corresponding to the turbidity maximum at the freshwater–seawater interface. The effect of the suspended load on percentage of dissolved metals is shown in Fig. 3B. Thereafter, dissolved As increased proportionately down the estuary and accounted for more than 90% of the total metal load at high salinities. Levels at the mouth of the Tamar, like Restronguet Creek, are comparable with oceanic levels and indicate only minimal transport to coastal waters under normal conditions. Occasionally, however, low-salinity water may extend beyond the mouth of the estuary

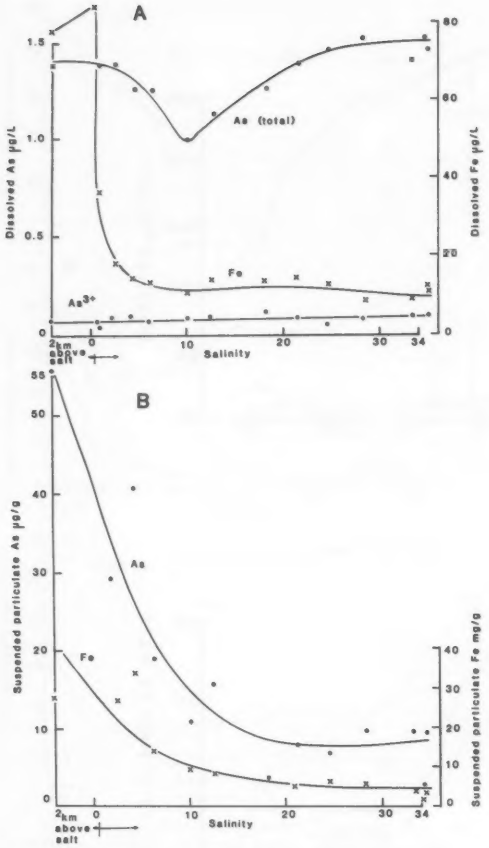

FIG. 5. Distribution of (A) dissolved metals and (B) particulate As and Fe in the Avon and its estuary.

causing elevated inputs of metals into coastal waters such as Plymouth Sound. Indeed, there is evidence to suggest that estuarine water may extend some considerable distance into the English Channel (Armstrong and Butler 1962).

AVON

Characterization of the fresh and salt water end members was simplified in the Avon Estuary due to the absence of significant metal inputs. Levels of dissolved As were between 1.4 and 1.5 µg/L in both types of water, typical values for areas free of As pollution. Nevertheless, nonlinearity of the total dissolved As mixing curve compared with the more conservative behavior of As^{3+} species indicates removal of 30% of the As^{5+} species at low salinities (Fig. 5A). Removal of more than 90% of the dissolved Fe also occurred in this region, as observed in other estuaries. Good correlations ($r^2 = 0.9756$) between particulate As and Fe (Fig. 2B and 5B) may again provide evidence of coprecipitation, and highest values were found upstream, in the region of removal. The Avon, like Restronguet Creek, has a fairly low-energy tidal regime, and resuspension of sediments is unlikely to be important in the cycling of metals compared with the Tamar Estuary.

As a result of the small amounts of suspended material in this estuary, and low levels of As contamination, the greatest proportion of As was dissolved, mainly as As^{5+} (Fig. 3C). The mean proportion of As^{3+} in these samples was 5.8 ± 1.7%.

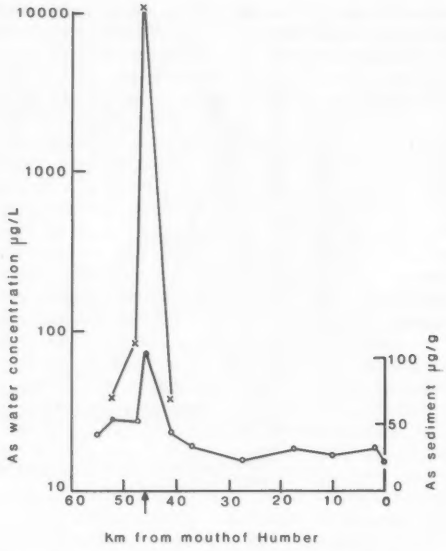

FIG. 6. Influence of waste from a metal refining plant (arrow) on levels of total As (particulate + dissolved) in the water column (×) and intertidal sediments (○) of the Humber Estuary.

HUMBER

It is interesting to compare the above results with those found in the Humber Estuary which receives effluent (containing up to 400 mg of As/L) from a metal refinery at a point source approximately 45 km from the mouth (Fig. 6). The restricted maximum for As concentrations, though highly significant, is clearly limited to a small area and is consistent with other observations of point-source discharges.

Discussion

The assessment of processes responsible for the transport and deposition of As and Fe in the estuaries studied is based on somewhat limited comparisons with hypothetical ideal mixing lines. Nevertheless, a consistent picture emerges which accounts for the observed behavior of these metals and which is supported by results from a continuing program of profiling.

Removal of "soluble" Fe in the low-salinity regions of Restronguet Creek and Tamar and Avon estuaries occurs by precipitation during the hydrolysis of hydrated Fe^{3+} and coagulation of riverborne Fe colloids in regimes of increasing ionic strength and pH values. Such behavior is a common phenomenon at the salt water interface in numerous estuaries (Windom et al. 1971; Boyle et al. 1977).

The data presented in this paper indicate that freshly precipitated colloidal hydrous oxides and hydroxides of Fe are important media for coprecipitation and removal of dissolved As. These processes are most significant where rapid hydrolysis of considerable quantities of Fe take place, such as in Restronguet Creek, or where high levels of suspended solids are encountered, as in the interface region of the Tamar Estuary. Although this behavior is predicted by the affinity of As ions for ferric hydroxide (Crecelius et al. 1975), As was unreactive in three southeastern U.S. estuaries, where complexes between As and low molecular weight dissolved organic matter may be more significant than As/Fe coprecipitation mechanisms (Waslenchuck and Windom 1978). It seems likely that under conditions of high dissolved organics (up to 55 mg/L) and extremely low As concentrations in these U.S. estuaries, the role of iron oxides as direct absorbants of metal ions may be overshadowed by competition from humic/fulvic-type compounds, compared with the less organic-rich waters of southwest England (up to 5.4 mg/L in the Tamar, 2.6 mg/L in the Avon). In view of the complex nature of Fe–humic interactions (Sholkovitz 1976), to imply As is associated totally with any particular phase may be an oversimplification. Nevertheless, analyses of chemical extracts of UK estuarine sediments show that 60% of the total As is usually associated with a readily extractable (1 *M* HCl) Fe/Mn oxide phase (Langston 1980). The highly significant correlations between As and Fe in these extracts therefore implies direct scavenging of As from solution by hydrous oxides of iron.

No other accounts of As reactivity in estuaries could be found; however, it is interesting to make comparisons with the behavior of other metals and nutrients in the Tamar and Restronguet Creek. Bryan (1980) has demonstrated removal of Cu and Fe at low salinities in Restronguet Creek, while more conservative dilution of Mn and Zn was observed during mixing. Removal of silicate and phosphate in the low-salinity region of the Tamar, possibly dependent on the amount of suspended particulate material present (Morris et al. 1981), may reflect processes in common with As removal described above. This view is supported in laboratory simulation experiments of Bale and Morris (1981) which demonstrate coagulation and precipitation of phosphate in association with removal of colloidal Fe at low salinities. Close comparison between arsenate and phosphate is expected as a result of their chemical similarities. In contrast, removal of Mn onto particulate phases, although an estuarine-induced phenomenon, occurs primarily in the freshwater region above the salt water interface. Extended maxima of Mn and ammonia in the mid-estuarine region of the Tamar (Bryan and Hummerstone 1973; Knox et al. 1981) were similar to As and may reflect common physical mixing processes of enriched pore and surface waters in this area.

The demonstration of coprecipitation of As and Fe in estuaries is of direct relevance to the assessment of biological availability. Previously (Langston 1980), it has been shown that As concentrations in estuarine bivalves are quantitatively related to sediment concentrations normalized to Fe content rather than As sediment concentrations alone. Drawing conclusions from the present study, As is partitioning predominantly to a substrate of high bonding strength (Fe oxides and hydroxides) resulting in specific As:Fe ratios in sediments. The presence of proportionately larger amounts of this strong bonding substrate in sediments should render the As less available to organisms. Surface-bound Fe is, therefore, an important factor affecting both the distribution and availability of As in estuaries.

To summarize, the removal process involving As and Fe described in this study indicates that estuarine sediments are important sinks for natural or anthropogenic inputs. Transfer to the oceans will, therefore, largely depend on the suspended load in outflowing waters, which may be small under normal conditions. Where resuspension of sediments does occur in estuaries, however, remobilization of dissolved As may contribute significantly to the cycling of this element.

Acknowledgments

I thank Mr G. Burt for help with collection and analysis of material and Dr G. W. Bryan for helpful discussions during the course of this work which was supported by United Kingdom Department of the Environment under contract DGR 480/51.

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The Distribution of Dissolved and Organically Complexed Copper and Nickel in the Middle Atlantic Bight[1]

ALFRED K. HANSON JR. AND JAMES G. QUINN

Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881, USA

HANSON, A. K. JR., AND J. G. QUINN. 1983. The distribution of dissolved and organically complexed copper and nickel in the Middle Atlantic Bight. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 151–161.

An analytical procedure involving C_{18} reverse-phase liquid chromatography and heated graphite atomizer–atomic absorption spectroscopy was used to isolate and measure dissolved organically complexed copper and nickel along a section from the shelf–slope boundary into the New York Bight apex. The dissolved organic matter isolated by C_{18} reverse-phase liquid chromatography was further separated and partially characterized by high-performance liquid chromatography. The distributions of dissolved copper and nickel were similar, with higher concentrations in the low-salinity surface waters and lower concentrations beneath the pycnocline and in slope waters. The concentration of total dissolved copper and nickel ranged from 0.77 to 8.67 nmol/kg and 2.3 to 14.7 nmol/kg, respectively. The concentrations of organically complexed copper (0.24–1.67 nmol/kg) increased uniformly across the shelf, with the highest concentrations at the New York Bight apex. A small percentage of the dissolved nickel (0–8%) was isolated as organically complexed nickel. The variation in the percentage of dissolved copper isolated as organically complexed copper (10–60%) was systematically related to other chemical properties and hydrographic features of the region. The organic components responsible for the copper complexation in these coastal waters are chromatographically similar to terrigenous fulvic acid and may originate in riverine waters.

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On a utilisé, pour isoler et mesurer le cuivre et le nickel complexés organiquement et dissous le long d'une coupe allant de la limite entre le plateau et la pente continentale, une méthode analytique impliquant la chromatographie en phase liquide inversée C_{18} et la spectroscopie d'absorption atomique avec atomiseur de graphite chauffé. La matière organique dissoute isolée par la chromatographie en phase liquide inversée C_{18} a été séparée davantage et partiellement caractérisée par chromatographie en phase liquide à haute performance. La distribution du cuivre et du nickel dissous est la même, les plus fortes concentrations se trouvant dans les eaux de surface de faible salinité et les plus faibles, au-dessous de la pycnocline et dans les eaux de pente. La concentration de cuivre et de nickel dissous totaux varie de 0,77 à 8,67 nmol/kg et de 2,3 à 14,7 nmol/kg respectivement. La concentration de cuivre complexé organiquement (0,24–1,67 nmol/kg) augmente de façon uniforme en travers du plateau, les plus fortes concentrations se trouvant au sommet de la baie de New York. Une petite portion du nickel dissous (0–8 %) a été isolée comme nickel complexé organiquement. La variation du pourcentage de cuivre dissous isolé comme cuivre complexé organiquement (10–60 %) est liée systématiquement aux autres propriétés chimiques et aux caractéristiques hydrographiques de la région. Les composants organiques responsables de la complexation du cuivre dans ces eaux côtières ressemblent chromatographiquement à de l'acide fulvique terrigène et peuvent avoir pour origine les eaux fluviales.

Received March 19, 1982
Accepted November 17, 1982

Reçu le 19 mars 1982
Accepté le 17 novembre 1982

[1]This paper forms part of the proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6858)
Imprimé au Canada (J6858)

KNOWLEDGE of the distribution and chemical speciation of trace metals in the oceans is required for an understanding of their role in various biogeochemical processes and evaluating the impact of anthropogenic metal inputs on the marine environment. Our understanding of the speciation of trace metals dissolved in seawater has been limited by a lack of information concerning the character and extent of the complexation of metal ions by dissolved organic matter (DOM). There is increasing evidence that metal–organic interactions are important to phytoplankton ecology (Sunda and Guillard 1976; Morel et al. 1978; Anderson and Morel 1978; Gavis et al. 1981), the enrichment of trace metals at the air–sea interface (Duce et al. 1972; Piotrowicz et al. 1972), the adsorption–desorption behavior of dissolved trace metals onto particles (O'Connor and Kester 1975; Davis and Leckie 1978; Hunter 1980; Balistrieri et al. 1981), and the exchange of metals between sediments and seawater (Sugai and Healy 1978; Lyons et al. 1979).

Investigations of the trace metal speciation of seawater usually involve two basic approaches: (1) the development of thermodynamic equilibrium speciation models based upon a knowledge of the chemistry of the metals and ligands and (2) the operational separation and measurement of the chemical species using physical and chemical analytical techniques. Thermodynamic speciation models predict that metal complexation by the DOM in seawater is particularly important for copper. This is mainly because copper(II) coordination complexes are more stable than those of other divalent transition metals (Stumm and Morgan 1970). Mantoura et al. (1978) predicted that, depending upon the humic ligand, 10–80% of the copper in seawater is complexed by humic substances. The formation of a rigorous equilibrium speciation model for trace metals in seawater has been hindered due to the lack of information on the type and concentration of organic ligands present in seawater and their complex formation constants with various metals. A variety of operational procedures have been employed for the measurement of organically complexed copper in marine waters. The general results, as reviewed by Mantoura (1981), indicate that an average of about 20% of the dissolved copper in seawater is organically complexed, with the percentage increasing in coastal and estuarine waters. Systematic comparison of kinetic and equilibrium speciation models with analytical data should ultimately result in an improved understanding of the trace metal speciation of seawater.

Recently, progress has been made in the development of analytical methods for the isolation and measurement of organically complexed copper in estuarine waters by C_{18} reverse-phase liquid chromatography (C_{18}-RPLC) combined with heated graphite atomizer–atomic absorption spectroscopy (HGA–AAS) (Mills and Quinn 1981; Mills et al. 1982). In this work the C_{18}-RPLC technique was applied for an investigation of the large-scale variability in the distribution of organically complexed copper and nickel in the coastal waters of the Middle Atlantic Bight.

Study Area

The Middle Atlantic Bight section consisted of seven stations running northwestward from the slope region across the continental shelf into the New York Bight apex (Fig. 1). The physical oceanography of this region has been studied by Bumpus (1973) and Beardsley et al. (1976). The Hudson and Connecticut rivers are the two largest sources of freshwater to the Middle Atlantic Bight. The Hudson River discharges directly into the New York Bight apex. The Connecticut River discharges indirectly into the bight at the eastern end of Long Island (Garvine 1975).

Man has significant impact on the water quality of the New York Bight. The bight waters are used for the disposal of a variety of wastes including dredge spoils, sewage sludge, industrial wastes, and sewage effluent. Klinkhammer and Bender (1981) studied the distribution of trace metals in the Hudson River estuary and concluded that sewage discharged from Manhattan and New Jersey contributed a fraction of the total flux of copper, nickel, and other metals that was comparable with the riverine source. The Marine Ecosystems Analysis (MESA) New York Bight project has accumulated considerable data on the water quality and chemical properties of the New York Bight (Alexander and Alexander 1977; O'Connor et al. 1977).

Methods

Sample Collection

Samples were collected during the Texas A&M R/V *Gyre* cruise No. 80-G6 during July 10–31, 1980. Seven depths were sampled at slope water station 13, and three depths (near surface, mid-depth, and near bottom) were sampled at shelf stations 14–19 (Fig. 1). Discrete water column samples were collected using acid-cleaned, Teflon-lined, 5-L Go-Flo bottles (General Oceanics) mounted on a CTD rosette. The water samples were transferred to 1-L Teflon bottles for immediate shipboard processing by the C_{18}-RPLC technique. Additional water samples for C_{18}-RPLC isolation of organic matter were collected from Narragansett Bay in 1-L Teflon bottles on April 2, 1980, by boat from the Connecticut River in 5-L Go-Flo bottles on July 10, 1981, and from the shore of the Hudson River in 1-L Teflon bottles on August 26, 1981.

Sample Processing

The method used for the isolation of DOM and metal–organic complexes was similar to that reported by Mills et al. (1982). The procedure employs a C_{18} SEP-PAK cartridge (Waters Associates, Milford, MA) as a chromatographic column. In practice, a reproducible characteristic fraction of the DOM, including organically complexed metals, is partitioned or adsorbed onto the C_{18} SEP-PAK. The isolated organic matter and associated metals are recovered by elution with a less polar solvent (methanol). The stationary phase of the C_{18} SEP-PAK is porasil (silica) that has nonpolar character because 18-carbon alkyl groups are chemically bonded to the silanol functional groups. About 350 mg of this material, with a particle size range of 75–80 μm, is packed into a linear polyethylene cartridge using a radial compression process which improves the quality of the chromatographic bed. We hypothesize that the contact time of the seawater with the C_{18} SEP-PAK chromatographic material (less than 1 s at a

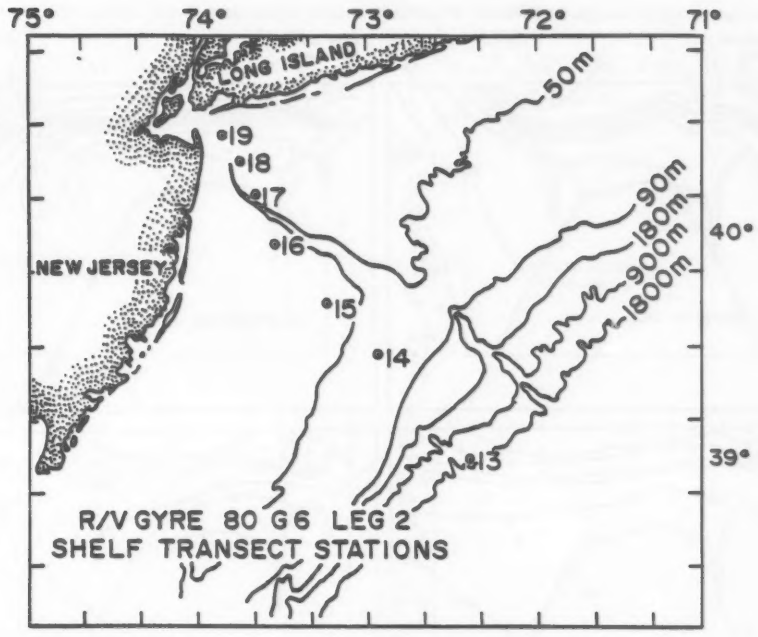

FIG. 1. Middle Atlantic Bight section including station locations.

flow rate of 15 mL/min) may be short relative to the time constants for significant shifts in the chemical equilibria of the more stable copper species in seawater (e.g. $CuCO_3^0$ and Cu−organic) (Zuehlke and Kester 1983).

The SEP-PAK cartridges were precleaned by successive rinsing with 20 mL of 0.6 mol HCl/L, 10 mL of Milli-Q deionized water, 20 mL of methanol, and 20 mL of Milli-Q deionized water. A custom-designed, plexiglass-enclosed, in-line nitrogen pressure filtration, C_{18}-RPLC system (Hanson 1981) was employed for rapid, contamination-free, shipboard sample processing. Six 1-L seawater samples were membrane filtered (0.4 μm, 47-mm Nuclepore polycarbonate) and passed through individual C_{18} SEP-PAKs in a single operation with this apparatus. A flow rate of 10−20 mL/min was employed. After processing, each SEP-PAK cartridge was rinsed with 5 mL of Milli-Q deionized water to remove salts, and the isolated organic matter and metal−organic complexes were eluted with 3 mL of methanol (Burdick and Jackson HPLC grade). An apparatus employing Teflon bottle reservoirs, Teflon tubing, and miniature, three-way Teflon valves (Hanson 1981) was required for contamination-free precleaning and elution of SEP-PAKs. The methanol eluates were collected in either Teflon or linear polyethylene (LPE) vials and stored at 0°C for future analysis. All plastic ware and filters that contacted the seawater samples and eluates had been acid cleaned and rinsed with Milli-Q deionized water.

Separate 250-mL samples of filtered seawater were collected in LPE bottles, acidified to pH 2 with 12 mol HCl/L (J. T. Baker, Ultrex), and stored for subsequent dissolved trace metal determinations.

TRACE METAL ANALYSIS

The C_{18}-RPLC methanol eluates were analyzed for copper and nickel by direct-injection HGA−AAS. A Perkin-Elmer model 603 spectrophotometer equipped with a model HGA 2100 graphite furnace and a deuterium arc background correction system was employed for the analyses. Trace metal standards prepared in methanol or 0.01 mol HCl/L had similar absorbances. HGA−AAS determinations of copper and nickel in methanol eluates by the method of standard additions confirmed the absence of matrix effects during direct-injection analysis. The limits of detection for organically complexed copper and nickel analyses were 0.02 nmol Cu/kg and 0.05 nmol Ni/kg, and typical relative standard deviations were 5 and 10%, respectively. The reagent blanks for both methanol and 0.6 mol HCl/L elution of precleaned SEP-PAKs were typically 0.05−0.08 nmol Cu/kg and <0.05 nmol Ni/kg.

Dissolved copper and nickel were preconcentrated from the 250 mL of seawater by coprecipitation with cobalt and ammonium pyrrolidine dithiocarbamate (APDC), using a procedure similar to that of Boyle and Edmond (1975). The pH of the acidified seawater was adjusted to 4.0 by the addition of 2.0 mL of 4.4 mol ammonium acetate/L. Two millilitres of 3.5 mmol cobalt chloride/L was added to the sample and the

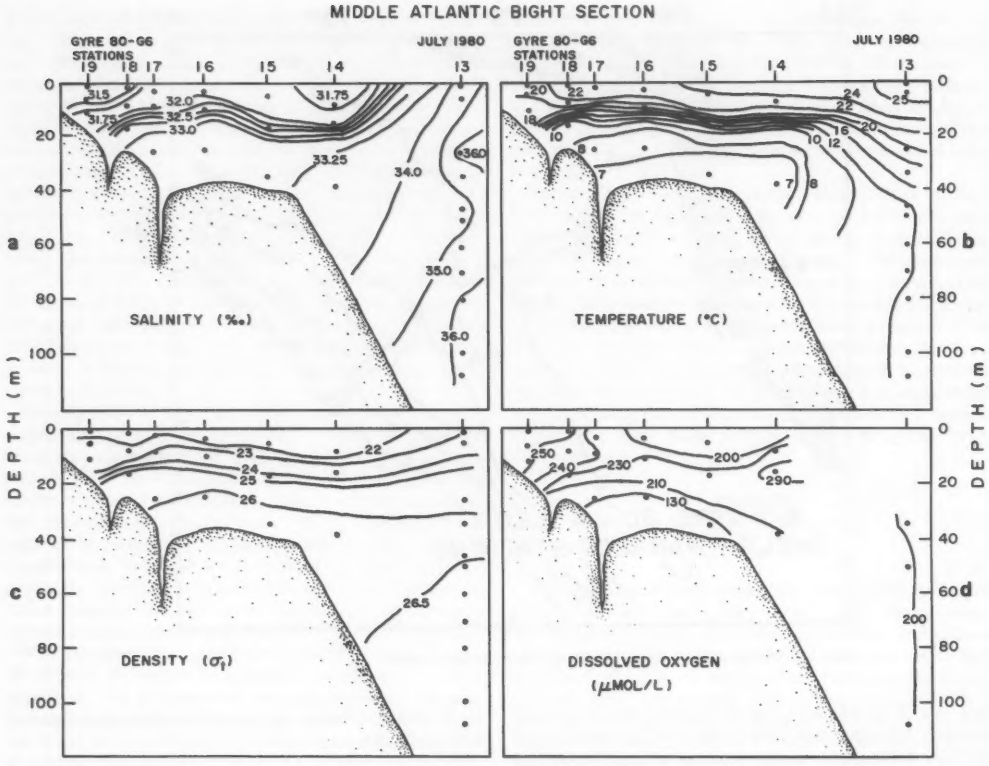

FIG. 2. Distributions of (a) salinity, (b) temperature, (c) density (σ_t), and (d) dissolved oxygen.

solution was mixed. Then, 2 mL of 0.1 mol APDC/L was added and the resulting precipitate was allowed to develop for 1 h. The cobalt–APDC precipitate containing concentrated metals was subsequently collected on a membrane filter (0.4 μm, 25-mm Nuclepore polycarbonate) by vacuum filtration, rinsed with Milli-Q deionized water, dissolved in 2 mL of 3 mol HNO_3/L (J. T. Baker, Ultrex), and stored in a LPE vial. The copper and nickel contents of these solutions were determined by HGA–AAS using trace metal standards prepared in 3 mol HNO_3/L. Typical procedural blanks were 0.2 nmol Cu/kg and 0.5 nmol Ni/kg, and the relative standard deviations of the copper and nickel determinations were 5 and 8%, respectively. All reported values have been blank corrected. The recoveries determined for copper and nickel additions to seawater samples were 98 and 99%, respectively.

Huizenga (1982) measured total dissolvable copper (unfiltered, acidified to pH 3) in a duplicate set of samples collected during the *Gyre* 80-G6 cruise. The copper results for the two data sets are significantly correlated (correlation coefficient = 0.971). There is an average 17% difference between the total and dissolved copper results that is partly (~10%) attributable to pH 3 dissolvable particulate copper.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC HPLC ANALYSIS

The organic matter isolated by C_{18}-RPLC, along with the complexed metals, was further separated and characterized by HPLC. A Waters Associates (Milford, MA) liquid chromatograph model ALC 244 was employed. It was equipped with two model 6000A pumps, a model 660 solvent programmer, a model 440 single wavelength (254 nm) UV detector, and a 300 × 3.9 mm (inside diameter) μ-Bondapak C_{18} reverse-phase column. The solvent system used for the HPLC analysis consisted of Milli-Q deionized water and acetonitrile (Burdick and Jackson HPLC grade). The pH of the aqueous phase was varied for different applications. The pH was adjusted to 3 by the addition of 1.2 mmol H_3PO_4/L and to 7.5 by the addition of 3 mmol K_2HPO_4/L and 0.87 mmol KH_2PO_4/L. A 1-h gradient elution was usually employed from 5% (v/v) acetonitrile in aqueous solution to 100% acetonitrile. Solvent flow rates were varied from 0.5 to 2.0 mL/min. The injection volumes of the methanol eluates were 100–300 μL. In certain cases, the methanol eluates were concentrated before HPLC analysis by evaporation

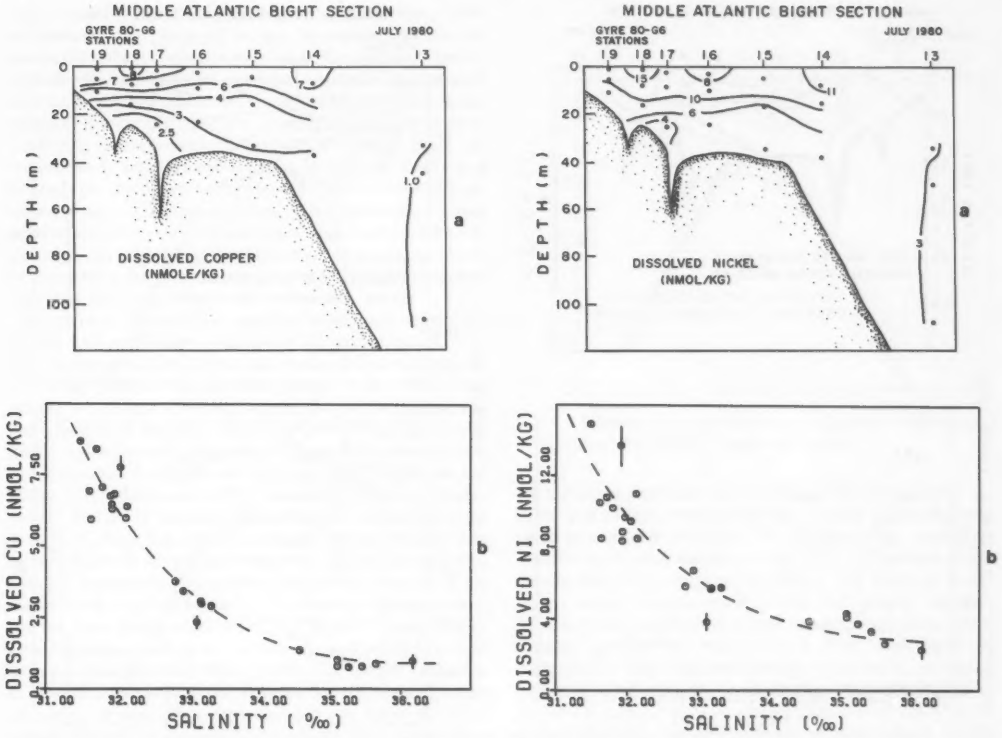

FIG. 3. (a) Distribution of dissolved copper and (b) plot of dissolved copper versus salinity.

FIG. 4. (a) Distribution of dissolved nickel and (b) plot of dissolved nickel versus salinity.

under nitrogen at 40°C.

Results and Discussion

The salinity, temperature, density (σ_t), and oxygen distributions for the section (Fig. 2) are characteristic of the shelf in the summer (Bowman and Wunderlich 1977). A strong thermocline developed resulting in a cool pool of isothermal, low-oxygen, bottom water extending across the shelf. This stratification allows the isopycnal communication of shelf water into the slope water region. Satellite infrared imagery indicated that slope water station 13 was located at the boundary of a warm-core Gulf Stream ring.

Dissolved Trace Metal Distributions

The concentrations of dissolved copper (Fig. 3a) and nickel (Fig. 4a) range from 0.77 to 8.67 nmol/kg and 2.3 to 14.7 nmol/kg, respectively. The warm low-salinity surface waters have higher dissolved copper and nickel concentrations than the cooler higher salinity shelf bottom waters and slope waters. Although this section is not a simple two end-member mixing system (Boyle et al. 1974; Officer 1979), the curvature of the dissolved metal versus salinity mixing diagrams (Fig. 3b and 4b) indicate that copper and nickel are being removed from the dissolved state during the continued mixing that occurs across the shelf. This removal is probably due to the incorporation of the metals into particulate phases by adsorption, biological uptake, or a combination of these as well as other mechanisms. The extrapolated 31‰ salinity end-member concentrations of dissolved copper (11 nmol/kg) and nickel (16 nmol/kg) are comparable with those estimated (16 nmol Cu/kg, 14 nmol Ni/kg) from the Hudson River estuary (0–31‰ salinity) concentration versus salinity plots of Klinkhammer and Bender (1981). The distribution clearly indicates that some dissolved copper and nickel of riverine and probably anthropogenic origin is transported across the shelf along density surfaces towards the slope water region during the seasonal period of stratification.

Boyle et al. (1981) suggested that copper enrichments observed in the shelf waters north of the Gulf Stream in July, 1979, may be due to nutrient trapping of copper that has been remobilized from mildly reducing shelf sediments. The data presented here suggest that shelf surface waters with elevated copper and nickel contents that originate from local riverine sources may extend well into the Atlantic slope water region

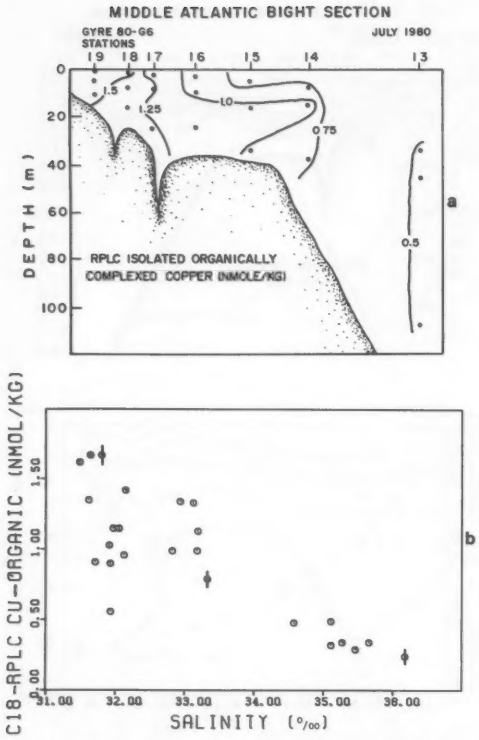

FIG. 5. (a) Distribution of organically complexed copper isolated by C_{18}-RPLC and (b) plot of C_{18}-RPLC organically complexed copper versus salinity.

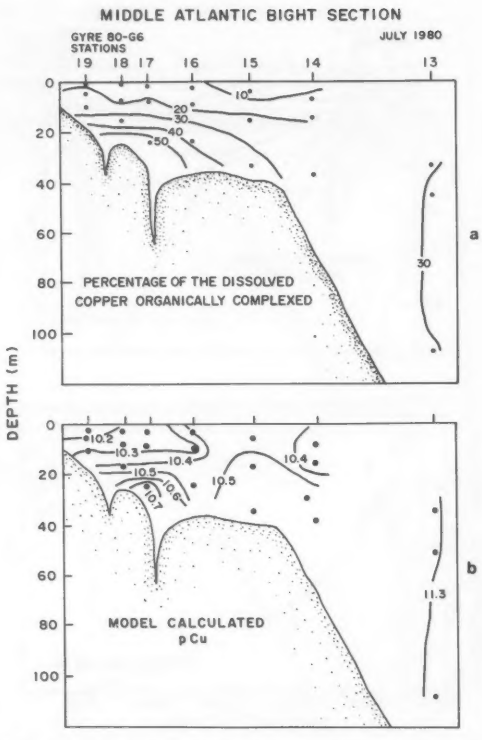

FIG. 6. Distributions of (a) the percentage of dissolved copper isolated by C_{18}-RPLC as organically complexed copper and (b) the model-calculated copper activity expressed as $pCu = -\log a_{Cu^{2+}}$.

in the summer and contribute to the observed enrichments in trace metals.

ORGANICALLY COMPLEXED COPPER DISTRIBUTION

The distribution of the C_{18}-RPLC isolated organically complexed copper (Fig. 5a) is not related in a simple manner to the distribution of dissolved copper or other hydrographic features. The concentrations of organically complexed copper (0.24−1.67 nmol/kg) decrease uniformly across the shelf, with the highest concentrations in the New York Bight apex. Although the concentration versus salinity mixing diagram (Fig. 5b) indicates that the distribution of organically complexed copper is generally correlated with the salinity (correlation coefficient = −0.890), there are systematic variations that are not salinity related. The water samples collected in the Middle Atlantic Bight may be classified into three water types according to their temperature-salinity (T, S) characteristics: (1) shelf surface water (S = 31.5−32.1‰, T = 16−24°C), (2) shelf subpycnocline water (S = 32.8−33.3‰, T = 6−16°C), and (3) slope water (S = 34.6−36.2‰, T = 7−16°C). The concentration of organically complexed copper varies considerably within the shelf surface waters (0.56−1.67 nmol/kg) and subpycnocline waters (0.79−1.34 nmol/kg) and is lower and less variable in the slope waters (0.29−0.49 nmol/kg) sampled.

A general explanation of the spatial distribution of organically complexed copper in the Middle Atlantic Bight results from the consideration of a recent model for the equilibrium speciation of copper in seawater (Zuehlke and Kester 1983). According to the model, the relative concentrations of the predominant dissolved copper species in seawater, copper carbonate ($CuCO_3^0$) and copper−organic complexes, are dependent upon the pH. Higher percentages of organically complexed copper species result at lower seawater pH values (within a pH range of 7.0−8.5), because less free carbonate ligands are available to compete for the copper ions than at higher pH. The pH of the bight waters generally ranges between 7.6 and 8.4 (Friedman et al. 1968). Higher pH values are typically found in near-surface waters. Lower pH values in summer subpycnocline waters have been attributed to the proximity of the sewage sludge dumping grounds and biochemical oxidation (Alexander and Alexander 1977). The percentage of the dissolved copper isolated as organi-

cally complexed (Fig. 6a) varied systematically from <10% in the outer shelf, high-pH surface waters to >50% in the lower pH subpycnocline waters near the Hudson Canyon (station 17). This variation in copper speciation is consistent with the model of Zuehlke and Kester (1983), and the concentration of organically complexed copper species measured by C_{18}-RPLC in the waters of the Middle Atlantic Bight are predictable (correlation measured vs predicted = 0.95) by a similarly designed model (Hanson 1981) in which the concentration of organic ligands is the only fitting parameter. These observations suggest that biological production and consumption can alter the copper speciation of marine waters to a considerable degree by simply forcing shifts in the carbonate equilibria and variations in pH.

It is widely believed that dissolved copper can control the growth and population composition of phytoplankton. The role of copper as a toxicant or micronutrient depends upon its chemical speciation in seawater (Davey et al. 1973). The toxicity of copper to several species of phytoplankton has been related to the free cupric ion activity in the growth media, and organically complexed copper is not directly toxic to phytoplankton (Sunda and Guillard 1976; Anderson and Morel 1978; Morel et al. 1978; Gavis et al. 1981). A characteristic feature of summer phytoplankton dynamics in the New York Bight has been the presence of the dinoflagellate *Ceratium tripos*. An unusual abundance of this phytoplankton species, beneath the pycnocline, is believed to be part of the causal chain of events that led to the observed summer anoxia off the New Jersey coast in 1976 (Falkowski et al. 1980). Dinoflagellates seem to be particularly susceptible to copper toxicity (Anderson and Morel 1978). The copper speciation model calculations (Fig. 6b) indicate that the higher fraction of copper organically complexed and the lower dissolved copper contents of summer subpycnocline shelf waters result in lower copper activities (higher $pCu = -\log a_{Cu^{2+}}$) relative to surface waters and may allow accelerated growth of *Ceratium tripos* at these depths.

The C_{18}-RPLC technique is unique in its approach to studying trace metal–organic species in seawater. Most other analytical speciation procedures evaluate the concentration of organically complexed metals from differences between analytical measurements made before and after modifications of the seawater (e.g. acidification, photooxidation, ion exchange). The C_{18}-RPLC method isolates the metal–organic complexes and allows their measurement and characterization. This technique may not be isolating all of the organically complexed copper present in seawater. It is not possible with available technology to assess unequivocally the total concentration of organically complexed copper in seawater. The C_{18}-RPLC technique removes up to 40% of the DOM (Mills et al. 1982), and this organic material complexes a significant fraction of the dissolved copper present in seawater. This fraction of the DOM may be that which is most geochemically significant for metal–organic interactions in seawater. Results obtained by C_{18}-RPLC must be evaluated by comparison with those of other operational procedures and theoretical speciation models.

Intercomparison of analytical methods for dissolved trace metal speciation requires an understanding of their operational character and is most informative when the techniques

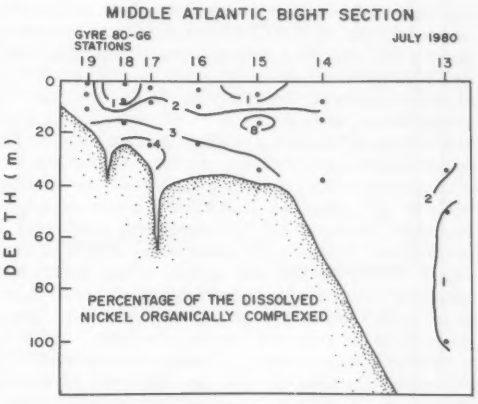

FIG. 7. Distribution of the percentage of dissolved nickel isolated by C_{18}-RPLC as organically complexed nickel.

are applied to equivalent water samples. Huizenga (1982) has developed a kinetic method for operationally estimating trace metal speciation in seawater. The "Chelex reactor" technique involves monitoring the removal rate of dissolved trace metals during batchwise agitation of Chelex 100 resin in a seawater sample. Labile metal species are readily removed from solution, and inert or bound metal species have slower removal rates. The results of a joint experiment on Narragansett Bay seawater (salinity = 31.14‰, dissolved copper = 27.2 nmol/kg) indicate that the concentration of C_{18}-RPLC organically complexed copper (7.0 nmol/kg) is comparable with the concentration of inert copper species (7.4 nmol/kg) that are not removed by the Chelex 100 resin after 100 h of agitation. Processing seawater by C_{18}-RPLC before Chelex reactor analysis removed most of the copper species that exhibited slower removal rates. This comparison suggests that the organically complexed copper isolated by C_{18}-RPLC is qualitatively and quantitatively similar to the operationally defined inert copper species estimated by the Chelex reactor method.

Organically Complexed Nickel Distribution

The concentration of organically complexed nickel isolated by C_{18}-RPLC varies from undetectable to 0.44 nmol/kg. Only a small percentage (0–7.6%) of the dissolved nickel was isolated as organically complexed (Fig. 7). Mantoura et al. (1978) investigated the interaction of nickel and humic material isolated from seawater by XAD-2 resin column chromatography. The results of their equilibrium nickel speciation model indicated that nickel would not be significantly complexed by humic material in coastal waters.

Characterization of the Metal Complexing Organic Matter

Understanding the causes of variations in the complexation of metals by DOM requires knowledge of both the metal and

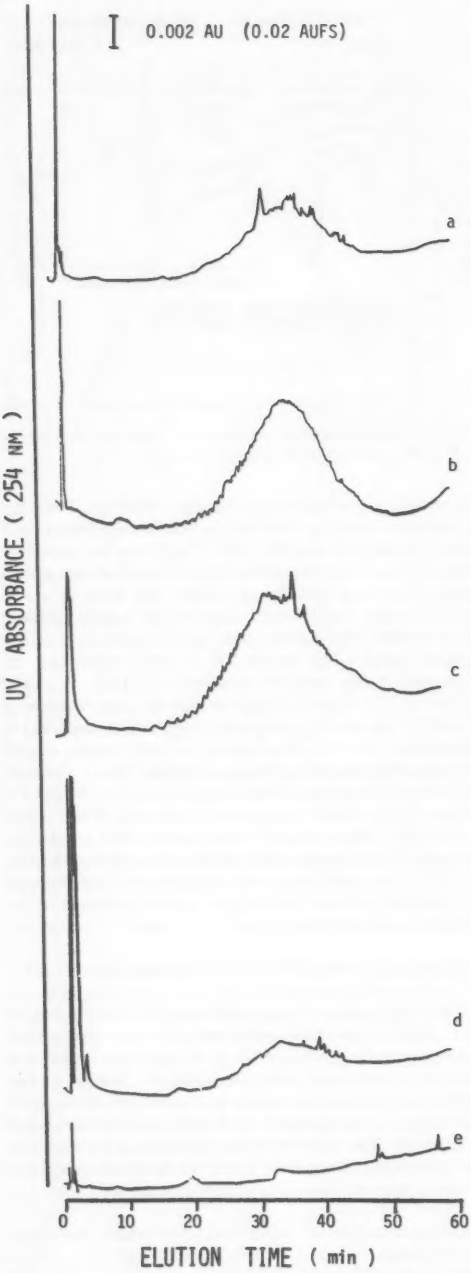

FIG. 8. HPLC profiles of (a) terrigenous fulvic acid, and DOM isolated by C_{18}-RPLC from (b) zero-salinity Connecticut River water, (c) station 14 shelf surface water, (d) station 13 slope water, and (e) procedural blank. An aqueous mobile phase of pH 3, a detector range of 0.02 AUFS (absorbance units full scale), and a flow rate of 2.0 mL/min were employed for the HPLC analysis. Other HPLC parameters were as described in the text.

the organic ligands involved. However, the origin, composition, and function of marine DOM has been the subject of numerous studies and despite these efforts, 80–90% of the DOM has remained uncharacterized. Many of the lower molecular weight compounds that have been identified in seawater (e.g. free amino acids) have the functionality required for metal complexation, but they may not be present in sufficient concentrations to significantly complex transition metals (Mantoura 1981). Dissolved macromolecular humic substances constitute a considerable fraction of the uncharacterized DOM (Stuermer and Harvey 1974) and have the ability to complex metals (Mantoura et al. 1978). Traditionally, humic substances have been divided into two operational fractions: fulvic acids (aqueous acid and base soluble) and humic acids (soluble only in aqueous base). The relative contribution and role of terrigenous DOM in the marine environment has been difficult to ascertain. Sholkovitz et al. (1978) demonstrated that 60–80% of riverine dissolved humic acids are flocculated during mixing in the Amazon Estuary. However, this removal accounts for only a small percentage (3–6%) of the total river DOM, which appears to mix conservatively with seawater. Riverine fulvic acids, with their smaller size and polar functionality, may be a major component of this DOM.

High-performance liquid chromatography is a promising technique for separating and characterizing the active metal complexing fraction of the DOM isolated from seawater by C_{18}-RPLC. The chromatograms in Fig. 8 and 9 represent the intensity of the UV absorbance at 254 nm of the conjugated and aromatic functional groups present in the organic matter eluting from the column with time as the mobile phase composition is varied from 5% (v/v) acetonitrile in aqueous solution to 100% acetonitrile. Organic components are generally expected to elute in order of decreasing polarity under these chromatographic conditions. Developments in HPLC methodology have demonstrated that reverse-phase columns, such as octadecylsilane (C_{18}), are suitable for the separation of weak organic acids and bases (Horvath et al. 1977). Chemical modifications to the aqueous mobile phase (e.g. pH buffering, ion pair formation, hydrophobic counter ion addition) may be employed to control the HPLC retention and selectivity of ionizable organic substances.

The chromatograms in Fig. 8 compare commercially available terrigenous fulvic acid (Contech E.T.C. Limited, Ottawa, Ont.) and organic matter isolated by C_{18}-RPLC from riverine and coastal marine waters. These chromatograms are characteristic of those obtained for water samples collected from the Middle Atlantic Bight, Narragansett Bay (Mills and Quinn 1981; Mills et al. 1981; Hanson 1981), and the Connecticut and Hudson rivers (Hanson 1981). The aqueous mobile phase was adjusted to pH 3 with H_3PO_4. This modification suppresses the ionization of weak organic acids, decreases their solubility in the aqueous mobile phase, and increases their HPLC retention time (Karger and Giese 1978).

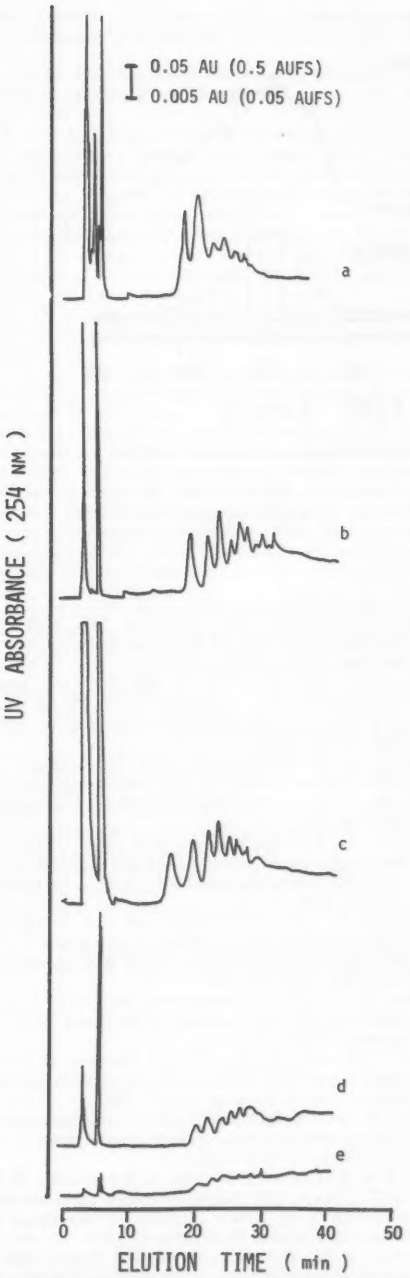

FIG. 9. HPLC profiles of (a) terrigenous fulvic acid, and DOM isolated by C_{18}-RPLC from (b) zero-salinity Hudson River water, (c) zero-salinity Connecticut River water, (d) station 13 slope water, and (e) procedural blank. An aqueous mobile phase of pH 7.5 and a flow rate of 0.5 mL/min were employed for the analysis. The detector range was 0.5 AUFS for the first 10 min and 0.05 AUFS for the remainder of the chromatogram. Other HPLC parameters were as described in the text.

Most of the UV-absorbing organic substances elute as a single unresolved complex mixture (UCM) of the intermediate polarity under these chromatographic conditions. The quantity of UV-absorbing organic matter isolated (as determined from the area of the UCM) decreased with increasing salinity in these coastal waters. When the mobile phase was buffered to pH 7.5 by the additions of KH_2PO_4 and K_2HPO_4, and the flow rate was reduced to 0.5 mL/min, the organic solute retention behavior was modified and resolution was improved. Chromatograms obtained under these conditions (Fig. 9) allow a more detailed comparison of the terrigenous fulvic acid with the organic matter isolated by C_{18}-RPLC from riverine and coastal marine waters. The coupling of HPLC with HGA–AAS allows the metal specific detection of eluting metal–organic complexes. The employment of HGA–AAS as an HPLC detector has recently been reviewed by Van Loon (1979) and has been applied for copper–organic complexes in river water (Lee 1981) and Baltic seawater (Kremling et al. 1981). The chromatogram presented in Fig. 10 was obtained under conditions designed to allow the HGA–AAS detection of the copper associated with the eluting organic matter that was isolated from Narragansett Bay seawater by C_{18}-RPLC. The mobile phase (pH 6) was not buffered or acidified. The chromatogram indicates that the copper is associated with the UV-absorbing organic substances that comprise the UCM and that the copper is distributed among a variety of sites within this organic material.

The seawater organic matter isolated by C_{18}-RPLC, which is chromatographically similar to terrigenous fulvic acid, has not been operationally separated into humic and fulvic acid fractions by traditional methods (Schnitzer and Kahn 1972; Stuermer and Harvey 1974). However, several lines of evidence indicate that this material may be classified as humic material that is similar to fulvic acid. (1) The protonation characteristics of the DOM isolated by C_{18}-RPLC are similar to fulvic acid (Mills et al. 1982). (2) The stability constant determined for copper–organic complexes isolated by C_{18}-RPLC (Zuehlke and Kester 1983) is comparable with that reported by Mantoura et al. (1978) for humic material isolated by XAD resin chromatography from river water and seawater. (3) Electron paramagnetic resonance (EPR) spectra of copper–organic complexes isolated by C_{18}-RPLC (Mills et al. 1982) have spin Hamiltonian parameter values that are similar to those reported for a fulvic acid–copper complex by Bresnahan et al. (1978). (4) The removal of the humic acids from riverine and estuarine waters, using an acidification and membrane filtration procedure similar to that of Sholkovitz (1976), did not remove the UV-absorbing, copper-complexing organic matter that is isolated by C_{18}-RPLC (Hanson 1981). (5) The quantity of UV-absorbing DOM isolated by C_{18}-RPLC and estimated by HPLC was conservative in Connecticut River estuarine waters and in laboratory estuarine mixing studies (Hanson 1981) over the

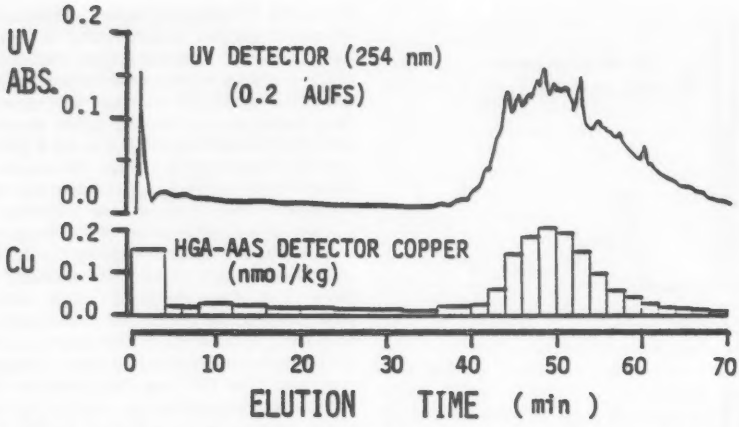

FIG. 10. HPLC profile of DOM isolated by C_{18}-RPLC from Narragansett Bay seawater (salinity = 30.0‰, dissolved copper = 47.6 nmol/kg, organically complexed copper = 12.6 nmol/kg). Copper was determined in the column eluent by HGA–AAS analysis of collected 1- or 2-mL fractions. An unbuffered aqueous mobile phase of pH 6, a flow rate of 0.5 mL/min, and a detector range of 0.20 AUFS were employed for the HPLC analysis. The volume of preconcentrated C_{18}-RPLC methanol eluate injected (0.01 mL) was equivalent to 0.42 kg of seawater.

0–30‰ salinity range. Sewage effluents contain humic substances that are similar to soil and riverine material. Characterization of these humic substances indicates that fulvic acid is a major component (Rebhum and Manka 1971). Investigations using C_{18}-RPLC in the Providence River and Narragansett Bay, Rhode Island, have indicated that sewage effluents are a major source of organically complexed copper to the bay (Mills 1981). These chromatographic results and other observations suggest that humic material, similar to terrigenous fulvic acid, that originates in riverine source waters and/or sewage effluents is present in sufficient concentration to significantly complex dissolved copper in the waters of the Middle Atlantic Bight.

Acknowledgments

We thank the scientific party and crew of the R/V *Gyre* cruise No. 80-G6 for assistance in sample collection and Dana R. Kester for kindly allowing participation in the cruise. We are also indebted to Carlton Hunt for the use of the atomic absorption instrumentation and to Gary Mills, Doug Huizenga, and Richard Zuehlke for helpful discussions. This research was partially supported by a grant from the Office of Naval Research (N0014-76-C-0226).

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Geochemical Transport Through the Miramichi Estuary[1]

D. E. BUCKLEY AND G. V. WINTERS

Environmental Marine Geology, Atlantic Geoscience Centre, Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

BUCKLEY, D. E., AND G. V. WINTERS. 1983. Geochemical transport through the Miramichi Estuary. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 162–182.

A 2-yr seasonal study of the physical oceanography, geochemistry, and sedimentology of the Miramichi Estuary, New Brunswick, demonstrated that the overall system consists of two compartments: a drowned river, variable salt wedge estuary which is normally highly stratified, and the connected Inner Bay which is slightly stratified to well mixed. Freshwater inputs at the head of the estuary vary from 50 to 250 $m^3 \cdot s^{-1}$ during summer and winter to high flows of 300 to 1700 $m^3 \cdot s^{-1}$ during spring. Suspended particulate matter (SPM) and several labile trace metals including Fe, Mn, Zn, Cu, Pb, and Cd were analyzed to determine the total transport of potential contaminants within the system and into the Gulf of St. Lawrence. Wide variations in concentrations of SPM and labile metal by more than an order of magnitude are a function of freshwater input rates, tidal prism flushing characteristics, and geochemical interactions within the estuary. The transports for SPM, particulate metals, and labile metals were calculated using a tidal prism flushing model. Although 70% of the annual input of SPM (95 000 t) is exported from the estuarine system, about 60% of the total Fe (2000 t) is trapped in the estuarine bottom sediments. By contrast, 50% more Mn (200 t) is exported in combined particulate and labile forms than is brought into the estuary by the river. The source of this additional Mn is remobilization from fine-grained reduced bottom mud. The most important sink for Fe, Zn, Pb, and Cd appears to be the organic-rich bottom muds of the upper estuary. During spring flood periods, which last for an average of 39 d, about 85% of the annual supply of SPM enters the river estuary from the Miramichi River. Also during this time, 30–55% of the annual supply of labile metals Fe, Mn, Zn, and Cu enter the system. Much of this spring influx of SPM and metal is remobilized in the estuary over the rest of the year.

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Une étude saisonnière de deux ans de l'océanographie physique, de la géochimie et de la sédimentologie de l'estuaire de la Miramichi, au Nouveau-Brunswick, a démontré que le réseau général comprend deux compartiments : un estuaire à embouchure ennoyé et à coin salé variable normalement fortement stratifié et une baie intérieure qui s'y rattache, allant de légèrement stratifiée à bien mélangée. Les arrivées d'eau douce de la tête de l'estuaire varient de 50 à 250 $m^3 \cdot s^{-1}$ en été et en hiver à des débits de 300 à 1 700 $m^3 \cdot s^{-1}$ au printemps. La matière particulaire en suspension (MPS) et plusieurs métaux en traces, y compris Fe, Mn, Zn, Cu, Pb et Cd ont été analysés en vue de déterminer le transport de contaminants potentiels dans le réseau et dans le golfe du Saint-Laurent. Les fortes variations de concentration, de plus de un facteur, dépendent des taux d'arrivée d'eau douce, des caractéristiques de vidange du prisme de marée et des interactions géochimiques au sein de l'estuaire. À l'aide d'un modèle de vidange du prisme de marée, nous avons calculé les transports de MPS, des métaux particulaires et des métaux labiles. Bien que 70 % des apports annuels de MPS (95 000 t) soient transportés hors du réseau estuarien, environ 60 % du Fe total (2 000 t) sont emprisonnés dans les sédiments benthiques de l'estuaire. Par contraste, 50 % plus de Mn (200 t) sont exportés sous formes particulaire et labile que la rivière n'en apporte à l'estuaire. Ce Mn supplémentaire est le produit d'une remobilisation de la fine vase du fond. Le plus important réservoir de Fe, Zn, Pb et Cd semble être les vases benthiques riches en matière organique du haut estuaire. En périodes de crues printannières, qui durent en moyenne 39 jours, environ

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6859)
Imprimé au Canada (J6859)

85 % des apports annuels de MPS pénètrent dans l'estuaire en provenance de la Miramichi. À cette époque également, de 30 à 55 % des apports annuels de métaux labiles Fe, Mn, Zn et Cu pénètrent dans le réseau. Une bonne partie de ces apports printanniers de MPS et de métaux est remobilisée dans l'estuaire le restant de l'année.

Received March 19, 1982
Accepted October 12, 1982

Reçu le 19 mars 1982
Accepté le 12 octobre 1982

SEDIMENTS from the drowned river channel of the Miramichi Estuary, New Brunswick, have significantly higher concentrations of trace metals than similar sized sediments from the Inner Bay regions (Willey and Fitzgerald 1980). These authors found that Mn, Zn, and Cu were strongly associated with the organic-rich sediments. Their findings demonstrated that the Miramichi sediments are contaminated with some metals that may be derived from urban and industrial effluents at the head of the estuary or from mining wastes which enter the drainage system well above the area of tidal influence.

In this paper we will present additional geochemical data on the concentration of trace metals in suspended particulate matter and on concentrations of total labile metal in the water. These data, obtained from samples collected throughout the estuary and at various times of the year between 1975 and 1977, will be related to the hydrologic conditions of the river freshwater inflow and to the physical oceanographic conditions within the estuarine system. Our objective is to demonstrate that geochemical transport of trace metals is quantitatively dependent on the partition between the solid and liquid phases and that estimates of metal fluxes can be obtained through the use of estuarine flushing models.

STUDY SITE

The Miramichi Estuary, located on the southwestern coast of the Gulf of St. Lawrence, serves as a hydrologic link between a 13 680 km^2 drainage area in New Brunswick and the open Gulf of St. Lawrence (Fig. 1). The estuary consists of two physiographic parts: (1) the Inner Bay, typical of a broad shallow bar-built estuary, is partially isolated from the Gulf by a series of Holocene age barrier islands and (2) a connecting drowned river channel, which is typical of a coastal plain estuary, extends westward for 10 to 40 km. The Inner Bay has a narrow navigation channel running through the centre which averages 6 m deep; otherwise, the water depth of the rest of the bay is generally less than 5 m. A meandering channel in the drowned river portion of the upper estuary is up to 15 m deep but accounts for less than one-half of the width of the upper estuary.

Rashid and Reinson (1979) recognized five major sedimentary environments on the basis of physiography in the estuarine system. Three of these environments are related to the hydrodynamics of the estuary inside the barrier islands. The meandering drowned river channel contains muddy sediments along the axis, with sands on the broad shoals and on the inside of meander bends. The Inner Bay contains a large central area in which muds predominate. Surrounding this central area are deposits of sandy mud and muddy sand grading outward to the east toward a large flood-tidal delta region in which sands are the dominant textural class.

Physical oceanographic observations and studies of the Miramichi Estuary began more than 40 years ago, but truly systematic examinations were begun only in the 1950's (Forthergill 1953; Bousfield 1955). In the last decade a number of detailed oceanographic studies were begun which provided the basis for modeling the oceanographic behavior of the estuary under various conditions of tide, freshwater runoff, wind, and ice cover. Data that included 10 000 pairs of salinity and current measurements from several of these studies (ComDev 1975; Transport Canada 1975; Krauel 1975; Winters and Buckley 1978) were used in a thorough analysis of the physical oceanography by Vilks and Krauel (1981).

Normally, the Miramichi Estuary is slightly stratified to well mixed in the Inner Bay area, whereas in the drowned river portion it is normally highly stratified. Variability in stratification is related to freshwater inflow conditions. The normal annual mean total inflow is 305 $m^3 \cdot s^{-1}$, but the monthly mean inflow may peak to six times the annual mean during the spring and may decline to $\frac{1}{10}$ the annual mean during summer and winter months (Ambler 1976). Under conditions of high freshwater inflow the variable salt wedge may penetrate less than 10 km into the drowned river channel section of the estuary. During these times parts of the upper estuary may become completely fresh, while the lower portion of the estuary becomes highly stratified. During periods of low river inflow the salinity intrusion may extend almost to the head of the tide, some 40 km up the river estuary. At these times the river estuary is less stratified (see Fig. 2a). There is not a significant increase in stratification in the Inner Bay with increased freshwater inflow, although there is a general reduction in salinity. Under ice-covered conditions, which begin in November or December and end in April, the water stratification increases throughout the system. This observation indicates that wind mixing, especially in the Inner Bay, may be a significant process.

The semidiurnal tide affects the depth of the halocline most profoundly in the drowned river channel, as might be expected (Vilks and Krauel 1981) (Fig. 2b). Under conditions of low-river inflow, tidal mixing was predominant in the river estuary. Tidal currents in the Inner Bay were usually rotary and counterclockwise under low freshwater inputs. In the river estuary, ebb currents were nearly always maximum at or near the surface and flood currents were maximum at middepths.

Sampling and Monitoring

Data presented here were obtained from analyses of samples collected during a multidisciplinary study of the Miramichi Estuary carried out between September 1975 and May 1977. In addition to the sampling program, more than 6000 in situ observations of salinity, temperature, current velocity, and turbidity were made throughout the field program. These

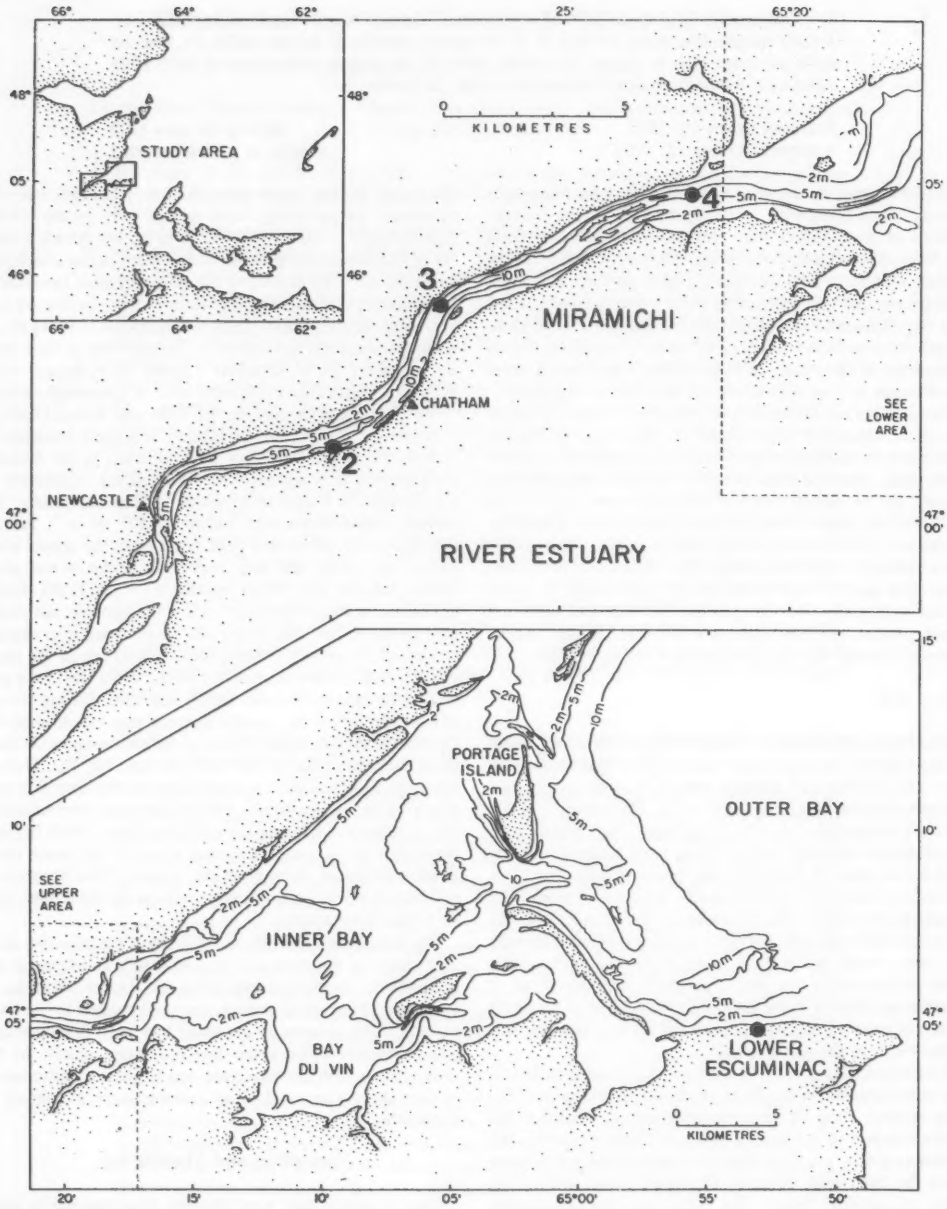

FIG. 1. Miramichi Estuary, located on southeast coast of Gulf of St. Lawrence (inset map).

data have been compiled together with some dissolved oxygen determinations and derived measurements of suspended particulate matter (SPM) in Winters and Buckley (1978). Turbidity measurements, obtained with an optical beam attenuance meter, were calibrated with water samples that were filtered to obtain gravimetric determinations of SPM (Winters

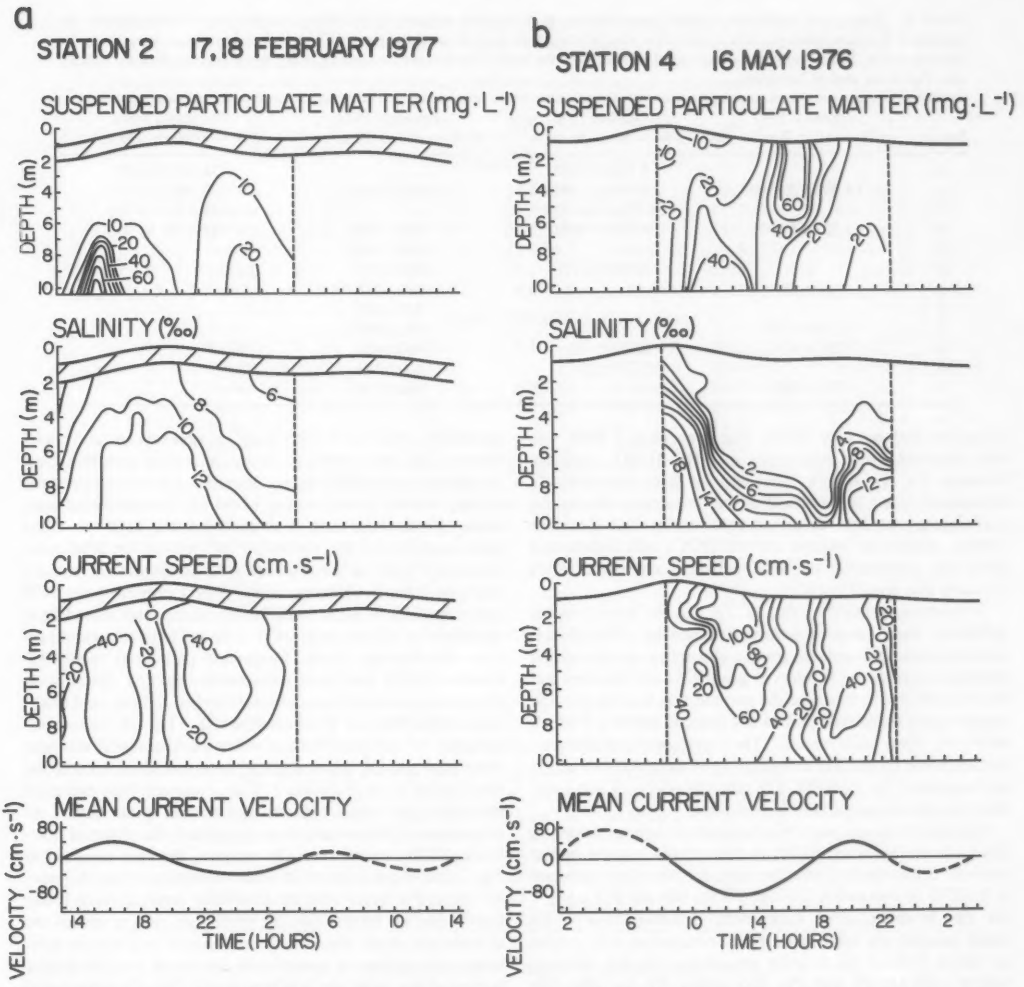

FIG. 2. Observed variations in SPM, salinity, and currents (a) at river estuary station 2 under ice-covered conditions and a freshwater inflow of 60 $m^3 \cdot s^{-1}$ and (b) at river estuary station 4 with a freshwater inflow of 1000 $m^3 \cdot s^{-1}$.

and Buckley 1980).

Sampling and monitoring stations were located throughout the Miramichi Estuary, extending from the upper estuary at the limit of tidal intrusion to the mouth of the Inner Bay where tidal channels through the barrier islands connect the Inner Bay with the Gulf of St. Lawrence. Seasonal sampling and monitoring stations (57 locations) were visited at various times of the year, with most intensive periods being September 1975, February 1976, May 1976, February 1977, and May 1977. Nine locations in the drowned river channel and the Inner Bay were reoccupied during several of these intensive sampling periods to determine variability associated with different freshwater inflows, with tidal stages, and with seasonal effects.

Water samples were obtained by pumping from two depths at each station, with repeated sampling every 3 h during one or two tidal cycles. Large-volume water samples were immediately subsampled for separation of samples for total SPM determinations and for total dissolved trace element analyses.

Laboratory Analytical Methods

Total SPM was separated from the water samples by vacuum filtration on 0.4-μm (pore size) Nuclepore microfilters

TABLE 1. Suspended particulate matter concentrations at monitoring stations in the Miramichi Estuary. Concentrations are expressed as micrograms per litre to facilitate comparisons with other data in this paper. FW signifies freshwater input from the drainage basin. Station numbers are arranged in order from the head of the estuary through the Inner Bay to the mouth of the estuary (see Fig. 3 for station locations).

Station	February 1977 (FW = 60 ± 2 $m^3 \cdot s^{-1}$)	October 1976 (FW = 50 ± 30 $m^3 \cdot s^{-1}$)	February 1976 (FW = 240 ± 20 $m^3 \cdot s^{-1}$)	May 1976 (FW = 1000 ± 200 $m^3 \cdot s^{-1}$)
1		5 960±5 262		24 247±8 073
2	15 090±20 300	5 000±2 101	8110±2503	20 198±24 052
3		42 730±49 328		14 678±13 403
4	3 521±3 140	5 250±5 891	4862±4836	12 945±10 358
18			1980±1612	
12		6 690±4 725	1550±2372	
8	310±58		980±283	
5			320±113	
9	2 318±1 972		1030±495	
6	215±90	2 535±672	900±424	
17		2 110±28	670±212	
7	327±128		960±1301	

(Cranston and Buckley 1972). The concentrated SPM was then digested using aqua regia and $HF–H_3BO_3$, and the elements Ca, Si, Al, Fe, Mn, and Zn were quantitatively determined using a modification of the atomic absorption spectroscopy method described by Buckley and Cranston (1971). Particulate organic carbon (POC) was determined from dry combustion of SPM collected on silver filters (Gordon and Sutcliffe 1973).

Seven trace metals (Fe, Mn, Al, Zn, Cu, Pb, and Cd) in the unfiltered water samples were determined by a chelation – solvent extraction and an atomic absorption spectroscopic method described by Winters et al. (1975) and Winters and Perkins (1975). In this case the method was used to provide results based on determinations at a reduced pH of 2.5 which represent "total labile metal." The extracted metal can also include some Fe and Mn mobilized from the reactive fraction of these metals on the SPM. The possible effects of this small addition are discussed later in this paper.

The analytical precision of all elemental determinations in solid silicate analyses (SPM) is 10% of the amount of the element determined. Detection limit for the major elements is 0.007% or less and is 2.0 $\mu g \cdot g^{-1}$ for Mn and 0.7 $\mu g \cdot g^{-1}$ for Zn. In the case of trace metal determinations in the water samples the total labile metal concentration is precise to within 15% of the amount present for Zn, Cd, and Cu, within 20% for Fe and Pb, and within 5% for Mn. The detection limit is 0.1 $\mu g \cdot L^{-1}$ for Fe and Mn, 0.06 $\mu g \cdot L^{-1}$ for Zn, 0.05 $\mu g \cdot L^{-1}$ for Cu, 0.005 $\mu g \cdot L^{-1}$ for Pb, and 0.001 $\mu g \cdot L^{-1}$ for Cd.

All of the analytical results for determinations of metals in water, suspended sediments, and bottom sediments, comprising about 10 000 data points, have been compiled by Winters et al. (1978). This paper will deal mainly with the trace metal data from this compilation and will emphasize aspects of SPM and water quality.

Distribution of SPM and Geochemical Composition

From a series of monitoring stations located throughout the estuarine system (see station locations in Fig. 3) SPM measurements were made over parts of tidal cycles at various times of the year (Table 1). It can be readily seen that great variability in total SPM occurs, in terms of both location in the estuary and the season during which the measurements were made. From these data it is apparent that both the mean concentration and the variability are highest for SPM measurements made in the drowned river portion of the estuary (stations 1 to 4). Winters (1981, 1983) examined the SPM concentrations in the drowned river channel and related these variations in SPM to stages of the tide and to freshwater inputs from the drainage basin. Suspended particulate matter responded to ebb and flood tidal current maxima. There is an obvious relationship between tidal current, salinity, and freshwater input (Fig. 2). The data depicted in Fig. 2b were representative of a period of the year when the river runoff was near maximum and the salt wedge had been forced seaward of the observation point at station 2. The strong ebb flow extended throughout the water column, and bottom scour caused resuspension of bottom sediments to produce the observed maximum SPM concentration. In contrast, the data depicted in Fig. 2a are representative of winter conditions when the estuary surface is frozen and the freshwater input is much lower than in spring. In this case the maximum current speeds are at midwater depth, the estuary is stratified, and bottom sediment resuspension is greatest on the flood tide. In a later section of this paper the distribution of SPM will be discussed in context with water transport mechanisms.

The amount of SPM varies with location in the estuarine system and with season of the year, as does its composition (Table 2). The SPM is organic rich and generally has a high Mn content (Table 2). Particulate organic carbon concentrations vary seasonally by as much as a factor of four. Particulate organic matter is usually higher in the more brackish surface water as compared with the near-bottom salt water. Variations in silicon and iron content are inverse to POC, indicating silicate dilution by particulate organic matter. This organic matter is primarily lignin material derived from the effluents of the pulp and paper industry located at the head of the estuary (Krank 1974; Rashid and Reinson 1979; Willey and Fitzgerald 1980). The influence of this organic matter on trace metal composition of the total SPM is complex. In the

TABLE 2. Composition of SPM collected from surface water and near-bottom water at selected stations in the Miramichi Estuary. Sampling was conducted over part of tidal cycle at various times of years. FW signifies freshwater input from drainage basin.

Station (Fig. 3)		Salinity (‰)	Si (%)	POC (%)	Fe (%)	Mn ($\mu g \cdot g^{-1}$)	Zn ($\mu g \cdot g^{-1}$)
			February 1977 (FW = 60 ± 2 $m^3 \cdot s^{-1}$)				
2	Surface	7.7±1.7	12.1±6.8	24.8±0.0	3.77±0.5	1083±160	209±48
	Bottom	11.2±2.3	20.5±1.5	10.3±9.2	4.02±0.1	1153±394	192±25
4	Surface	12.8±1.9	11.7±3.7	31.8±20.3	2.80±0.8	1453±1335	234±80
	Bottom	22.1±2.6	20.2±2.3	13.9±5.7	3.94±0.6	2096±378	196±43
9	Surface	24.8	12.9	67.1	2.63	2090	111
	Bottom	27.4±0.0	23.1±0.5	8.6±0.6	4.37±0.1	1735±318	134±6
			October 1976 (FW = 150 ± 30 $m^3 \cdot s^{-1}$)				
1	Surface		16.5±3.8	8.1	4.92±0.8	3693±214	899±218
	Bottom		17.3±2.3		4.22±0.6	3110±537	756±586
2	Surface	6.5±2.0	16.7±2.4	8.9±0.4	4.18±0.2	5499±1094	321±70
	Bottom	15.1±3.7	19.9±2.7	5.7±2.3	3.76±0.3	3998±1455	230±41
3	Surface		21.0		4.0	1440	251
	Bottom		20.6		4.5	5890	381
4	Surface	13.3±3.1	16.1±1.5	15.0±10.6	3.87±0.4	6432±1111	336±103
	Bottom	23.1±0.8	19.4±2.0	9.3±4.0	3.08±0.6	2698±785	238±70
12	Surface		24.3±0.9	18.9	3.38±0.1	4870±3889	732±479
	Bottom		25.9		3.43	1920	423
6	Surface		19.1		2.52	5050	741
	Bottom		18.3		2.40	2640	930
17	Surface		18.9		2.21	3860	550
	Bottom		17.2		1.84	2640	791
			February 1976 (FW = 240 ± 20 $m^3 \cdot s^{-1}$)				
2	Surface		3.9		1.0	260	373
	Bottom		22.2		3.77	600	225
4	Surface						
	Bottom	18.7±2.9	22.1±6.2		4.06±0.7	710±213	321±120
			May 1976 (FW = 1000 ± 200 $m^3 \cdot s^{-1}$)				
1	Surface	2.5±0.3	20.9±4.2	20.6±5.0	4.49±0.7	1212±239	302±118
	Bottom	2.7±0.4	21.3±3.7	12.6±1.9	4.35±0.9	1205±314	259±149
2	Surface	0.3±0.2	18.1±1.9	19.2±7.0	4.25±0.5	857±277	414±151
	Bottom	12.8±9.2	18.8±8.4	18.0±4.9	3.50±1.9	818±368	326±65
3	Surface	0.8±0.4	17.1±2.9	17.7±0.8	4.52±0.3	633±167	226±143
	Bottom	10.1±0.3	19.6±2.2	15.7±1.6	4.56±0.4	763±182	275±72
4	Surface	2.9±0.7	19.4±1.6	25.5	4.38±0.5	873±395	361±59
	Bottom	20.2±1.4	19.9±2.6	14.7±0.5	4.37±0.5	868±373	343±111

brackish water of the upper estuary there is no apparent association of the Mn and organic matter in the SPM; however, in the central estuary there is a positive correlation ($r = 0.552$, $n = 16$, $P > 95\%$) between POC and particulate Mn. The Zn concentration in SPM also correlated positively with POC ($r = 0.555$, $n = 34$, $P > 99.9\%$) throughout the estuary.

Trace Metals in Water

The concentration of total labile metal in unfiltered water samples collected from the monitoring stations is highly variable. The highest concentration of labile metal is found in the upper estuarine areas (Table 3). However, the rate of decrease in metal concentration with distance from the head of the estuary is not uniform for all six of the trace metals. Furthermore, the dispersion of labile metal in the upper river estuary is highly dependent on the rate of freshwater input and the degree of salinity stratification.

A series of multivariable linear regression analyses were conducted which related the composition of the SPM and the salinity of the water samples to the measured concentration of labile trace metals. To carry out these analyses the composition data for the SPM was converted to particulate concentration (micrograms per litre). The trace metals Cu, Pb, and Cd were not determined in the SPM, so direct comparison could not be made between these metals in the particulate form and the total labile concentration.

The results of the multiple regression analyses for Fe demonstrate that 10% of the particulate Fe concentration contributed to the total labile Fe concentration and that the labile Fe decreases as the salinity increases by the relationship (95% confidence interval) labile Fe = (78 ± 15) + (0.10 ± 0.01) particulate Fe − (3.3 ± 0.7) salinity ($N = 61$, overall $r = 0.936$). For this as well as following regression relationships

TABLE 3. Concentration of total labile trace metals in surface and near-bottom water at selected stations in the Miramichi Estuary. Sampling was conducted over part of tidal cycle at various times of years. FW signifies freshwater input from the drainage basin.

Station (Fig. 3)		Fe ($\mu g \cdot L^{-1}$)	Mn ($\mu g \cdot L^{-1}$)	Zn ($\mu g \cdot L^{-1}$)	Cu ($\mu g \cdot L^{-1}$)	Pb ($\mu g \cdot L^{-1}$)	Cd ($\mu g \cdot L^{-1}$)
				February 1977 (FW = 60 ± 2 $m^3 \cdot s^{-1}$)			
2	Surface	113±32	70±24	2.84±1.3	0.49±0.1	1.16±0.3	0.029±0.01
	Bottom	173±86	51±16	3.21±0.7	0.56±0.3	1.65±0.9	0.026±0.02
4	Surface	37±4	53±16	3.62±1.2	0.29±0.05	0.28±0.4	0.013±0.01
	Bottom	47±23	23±10	3.02±0.7	0.30±0.06	0.03±0.01	0.019±0.01
8	Surface	7.7±5.2	18±12	2.30±1.0	0.22±0.01	0.03±0.01	0.020±0.01
	Bottom	5.2±1.8	6.4±3.3	1.50±0.4	0.21±0.01	0.03±0.01	0.018±0.01
9	Surface	29±34	12.3±3.4	1.80±0.1	0.23±0.01	0.02±0.00	0.032±0.004
	Bottom	25±17	8.2±1.8	1.80±0.1	0.24±0.02	0.03±0.01	0.032±0.004
6	Surface	6.5±4.0	12.9±4.6	2.60±1.3	0.26±0.05	0.03±0.01	0.019±0.01
	Bottom	4.4±2.1	6.0±0.7	1.30±0.1	0.22±0.00	0.03±0.01	0.024±0.02
7	Surface	8.7±5.6	2.0±0.1	1.40±0.4	0.25±0.04	0.03±0.01	0.031±0.03
	Bottom	3.4±4.1	2.1±1.1	1.00±0.1	0.19±0.03	0.02±0.00	0.020±0.01
				October 1976 (FW = 150 ± 30 $m^3 \cdot s^{-1}$)			
1	Surface	83	44	28	0.75	2.00	0.071
2	Surface	69±8	54±3.5	5±2.7	0.67±0.12	0.43±0.0	0.049±0.004
	Bottom	32±15	21±7.8	1.80±0.0	0.67±0.01	0.40±0.5	0.077±0.05
4	Surface	39±16	30±14	2.00±0.5	1.96±2.30	0.14±0.11	0.045±0.02
	Bottom	27±24	11±5	1.30±0.4	0.77±0.74	0.10±0.06	0.059±0.02
12	Surface	4.0	3.9	1.10	0.43	0.02	0.034
				February 1976 (FW = 240 ± 20 $m^3 \cdot s^{-1}$)			
4	Surface	45±8	20.4±0.8	4.60±0.8	0.41±0.16		
	Bottom	43±16	12.7±4.0	3.80±1.0	0.31±0.15		
18	Surface	43	33	3.30	0.29		
	Bottom	20	7.3	2.00	0.21		
12	Surface	30	31	3.50	0.24		
	Bottom	8.8	4.4	1.70	0.21		
8	Surface	27	33	3.60	0.31		
	Bottom	4.8	11.4	1.50	0.10		
5	Surface	123	53	6.50	0.36		
	Bottom	6.5	4.2	2.20	0.22		
9	Surface	22	29	3.10	0.21		
	Bottom	3.7	1.1	1.40	0.13		
6	Surface	30	22	5.60	0.38		
	Bottom	9.8	6.8	2.20	0.18		
17	Surface	17	16	1.90	0.13		
	Bottom	5.2	7.7	1.00	0.10		
7	Surface	13	8.5	2.50	0.13		
	Bottom	6.6	1.0	0.60	0.10		
				May 1976 (FW = 1000 ± 200 $m^3 \cdot s^{-1}$)			
1	Surface	145±41	27±3.1	5.13±0.67	1.56±0.25	0.12±0.07	0.248±0.30
	Bottom	173±37	34±12	5.37±1.21	1.51±0.13	0.17±0.07	0.075±0.004
2	Surface	89±41	29±2.7	2.89±0.26	0.73±0.17	0.29±0.35	0.020±0.01
	Bottom	204±132	42±16	3.15±0.67	1.07±0.51	2.42±2.71	0.027±0.01
3	Surface	105±83	26±15	3.15±1.35	1.01±0.35	0.02±0.01	0.033±0.02
	Bottom	140±109	33±16	3.62±1.74	1.08±0.46	0.11±0.11	0.041±0.01
4	Surface	77±75	25±8	3.60±1.57	0.88±0.32	0.08±0.03	0.074±0.04
	Bottom	135±51	11±2.6	3.23±1.69	0.55±0.04	0.13±0.03	0.044±0.04

all concentrations are in micrograms per litre, except for salinity (‰).

A similar analysis of Mn data produced two different relationships for data sets representing different monitoring periods. When the freshwater input was at average or moderately low rates, the total labile Mn could only be related to salinity as labile Mn = (78 ± 8) − (2.7 ± 0.4)salinity (N = 63, r = −0.862). During the spring flood when total SPM was high throughout the river estuary, the labile Mn concentration was related to the POC concentration and the salinity as labile Mn = (21 ± 5) + (0.004 ± 0.001)POC − (0.9 ± 0.4)salinity (N = 32, overall r = 0.830). These data were all

obtained from the river estuary at a time of year when the salinity range was low (see Table 2). There was no significant correlation between particulate Mn and labile Mn. This would suggest that only the Mn associated with the organic matter contributed to the total labile Mn in the spring flood period, and this Mn was a small proportion of the total particulate Mn.

The relationship between total labile Zn, SPM, and salinity also included an indication of some association with POC: labile Zn = (3.2 ± 0.5) − (0.06 ± 0.03)salinity + (0.0003 ± 0.0001)POC (N = 88, overall r = 0.696). This relationship was somewhat less significant as compared with Fe and Mn but was still highly significant ($\alpha < 0.0005$).

An association between total labile Cu and POC is indicated by a small contribution from the POC term: labile Cu = (0.74 ± 0.11) + (0.00012 ± 0.00003)POC − (0.019 ± 0.005)salinity (N = 87, overall r = 0.872).

Although both of the metals Pb and Cd were most concentrated in the upper estuarine water there was no statistically significant correlation between the labile metal concentration and SPM or the salinity of the water.

Estuarine Transport of Water Quality Parameters

We demonstrate that SPM and total labile metal concentrations vary with season and with changing freshwater inputs. Water quality parameters vary with geographic location throughout the estuarine system, and this variability is probably related to saline and freshwater mixing as well as to some chemical interaction with the suspended particulate matter. We discuss these variations with respect to a tidal prism flushing model to estimate the quantitative transport of these water qualities.

Vilks and Krauel (1981) applied a tidal prism flushing model (Ketchum 1951) to the Miramichi system to estimate the freshwater fraction in various segments. They defined segments of the Miramichi Estuary based on the freshwater inflow. The first segment, located at the head of the tide, was defined as being equal in volume to the freshwater inflow volume per tidal cycle. Each succeeding segment progressing seaward contains a high-tide volume equal to the low-tide volume in the adjacent seaward segment. Assuming complete mixing within each segment an exchange ratio was calculated for each segment based on the low and intertidal volume of each segment. They then calculated the freshwater fraction of the total volume of each segment using the exchange ratio and the volume of freshwater in each segment. This calculated freshwater fraction could then be compared with the freshwater fraction, FW_f, calculated from salinity observations:

$$FW_f = \frac{Sb - \bar{S}}{Sb}$$

where Sb is the base salinity from outside the estuary and $\bar{S}$ is the mean salinity observed in the segment. There are some limitations to the use of this modeling approach as pointed out by Vilks and Krauel (1981). These are due to salinity stratification and lack of complete vertical and horizontal mixing within each segment. Also, SPM is not expected to be uniformly distributed throughout the water column. In spite of these limitations, our calculations include SPM and total labile metal concentrations so that departures from predicted values (calculated from model) can be interpreted in terms of anomalous inputs or possible geochemical interactions.

A flushing model based on the mean river inflow for each of the four seasonal monitoring periods (see Fig. 6) will be discussed below. For these periods the mean river input varied from 60 $m^3 \cdot s^{-1}$ for February 1977 to a high of 1000 $m^3 \cdot s^{-1}$ for May 1976. The resulting segment lengths, equal to the horizontal tidal excursion, for each model are depicted in Fig. 3. In addition, we have included a model that represents the mean annual inflow condition of 305 $m^3 \cdot s^{-1}$ (Fig. 4). The observed freshwater fraction was derived by taking 28.0‰ as the base salinity and using the formula explained above.

The observed salinities (or freshwater fractions) and predicted values (Table 4) are in best agreement for box segments located in the Inner Bay. The departure in the upper river estuary is likely due to the lack of vertical mixing in that area. Salinities in the river estuary are generally lower than predicted, except for conditions when the river inflow is very high. Under high freshwater inflow conditions the halocline is very steep and the salt wedge is pushed seaward. Thus, larger variations in average volume salinities can be anticipated during high river inflow.

Observed concentration factors (C_f) for SPM, POC, and total labile metal at each station are given in Table 5 with the observed freshwater fraction (FW_f), which is computed from observed salinities and the river input concentration, C_r, for zero salinity. The concentration of SPM, POC, and labile metals at each of the model segments can be derived as a product of C_r and C_f. If the mean observed concentration factor, $\bar{C}_f$, for any parameter exactly corresponds to FW_f, then this signifies that the water quality parameter is conservative with respect to freshwater mixing with salt water.

Departures from a simple saltwater mixing model can be graphically illustrated using differences in concentration factors along the estuary with respect to the observed salinity or the freshwater fraction FW_f. Thus, $\Delta\bar{C}_f = \bar{C}_f - FW_f$ is plotted on the vertical axis of Fig. 5. Generally, SPM and POC diverge widely from the conservative nature of the ideal mixing model, as expected. The highest concentration factors for SPM and POC occur in the upper estuary, suggesting that the peak concentration factor moves down the estuary as the freshwater input increases. This observation is consistent with turbidity maximum models suggested by Allen et al. (1980) and Avoine et al. (1981) in which the maximum turbidity zone occurs at the zone of maximum turbulence between the front of the salt wedge and the counter flowing freshwater. A second probable cause of the high turbidity in the river estuary is the injection of SPM and POC from the pulp and wood fiber industries located near the head of the estuary. In particular, the very high POC factors are attributed to these industries as previously pointed out by Willey and Fitzgerald (1980) and Rashid and Reinson (1979). A secondary increase in SPM and POC is found in the centre of the Inner Bay (Fig. 5, stations 8, 9, and 12). This increase may be due to resuspension under the influence of strong winds blowing across the shallow bay, as occurred in October 1976, or may be due to strong flood currents sweeping across unstable mud deposits (Reinson 1976; Schafer et al. 1977).

The three labile trace metals (Fe, Mn, Zn) in Fig. 5 depict various relationships to the associated SPM, POC, and

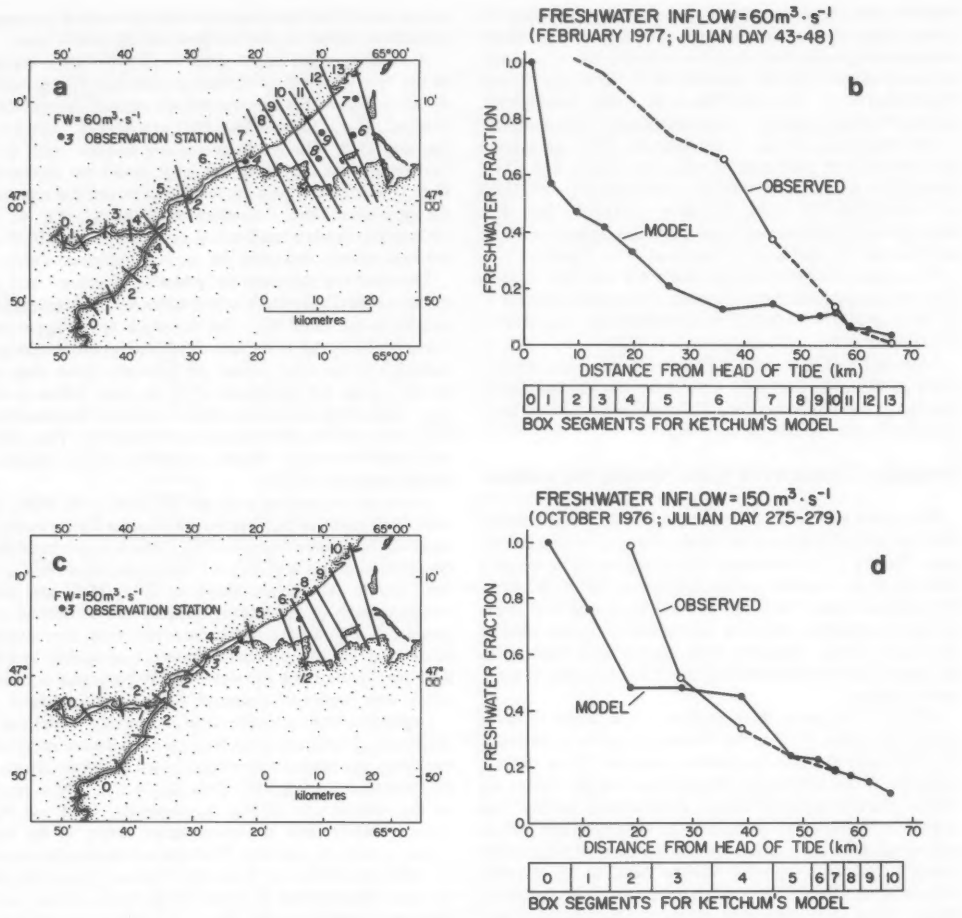

FIG. 3. (a, c, e, g) Distribution of box segments of Ketchum (1951) tidal prism flushing model for various freshwater inflow rates. The monitoring stations shown in this figure were used to obtain mean observed water quality data over one or more tidal cycles: (a) 60 $m^3 \cdot s^{-1}$; (c) 150 $m^3 \cdot s^{-1}$; (e) 240 $m^3 \cdot s^{-1}$; (g) 1000 $m^3 \cdot s^{-1}$. (b, d, f, h) Freshwater fractions for each segment of the Ketchum (1951) tidal prism flushing model. Observed freshwater fractions were determined from mean salinity observed at stations located in boxes shown in (b) Fig. 3a, (d) Fig. 3c, (f) Fig. 3e, and (h) Fig. 3g.

estuarine mixing. Total labile Fe closely parallels the trends in total SPM. As previously pointed out, 10% of the particulate Fe contributed to the labile Fe. The trend with Mn is more complex although it generally follows the trend of POC. Reduction of total labile Mn appears to occur in February 1977. In the presence of very high POC the Mn becomes complexed with organic matter which is not dissociated under the conditions of low pH extraction. The comparison between Zn and POC also suggests some control of labile Zn by the organic matter, but in this case the patterns are not as clearly defined.

Further analyses of deviation from conservative mixing of SPM, POC, and the labile trace metals were undertaken after correcting for saltwater end member contributions. The residual concentrations, ΔC, for each box model segment was then determined as follows:

$$\Delta C = \bar{C} - C_0(1 - \mathrm{FW}_f) - C_r \times \mathrm{FW}_f.$$

For each water quality, C_0 is the observed or extrapolated base concentration in the seawater end member with a salinity of 28‰. These ΔC values are compiled in Table 6.

In the upper estuary the contribution of "excess" SPM to the

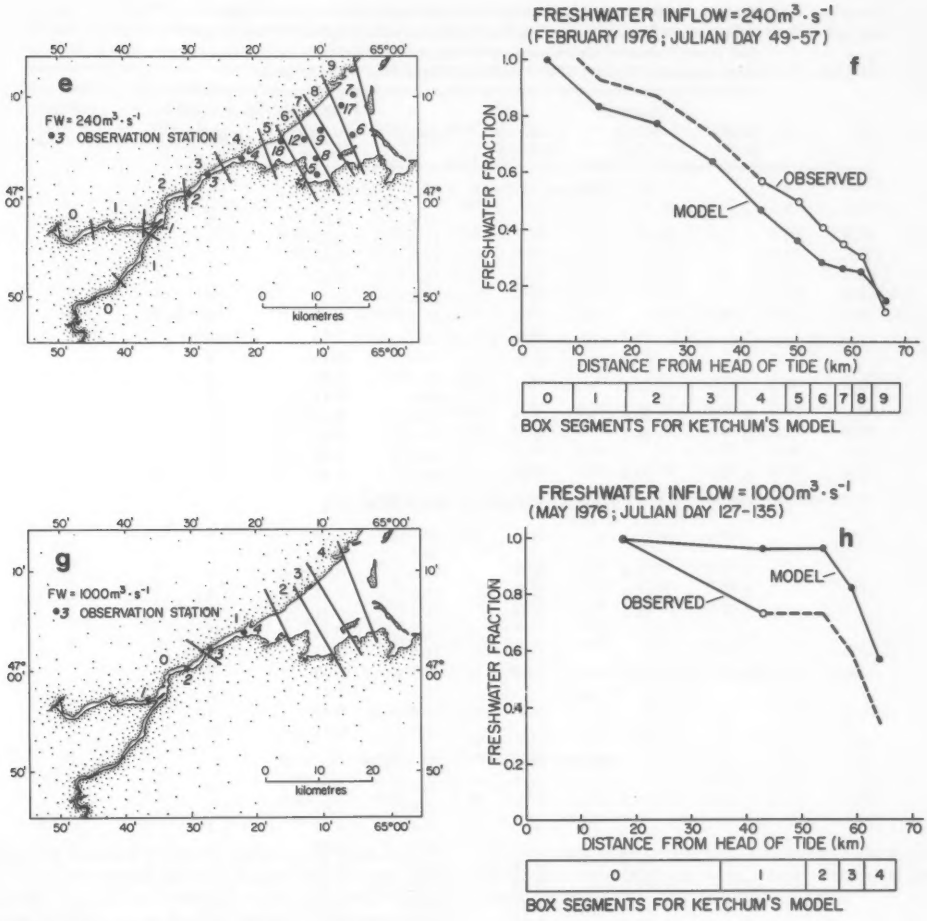

FIG. 3. *(Concluded).*

water column varies from 10 to 70%. Similar contributions of POC are also evident, but some surprising gains are evident in samples from the Inner Bay. This may be due to resuspension of low-density lignin from bottom sediments and some additions of planktonic matter from the surface waters. Rashid and Reinson (1979) have noted the mixing of marine organic carbon and terrestrial organic matter in bottom sediments from the Inner Bay. The negative ΔC values indicate that the observed concentrations are lower than expected and indicate that some removal process was responsible. For

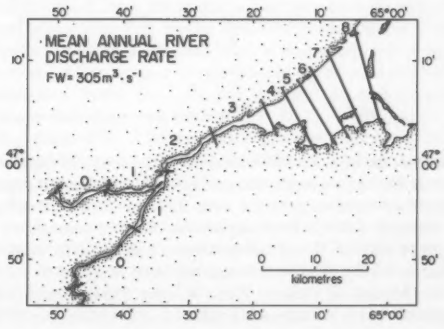

FIG. 4. Distribution of box segments of Ketchum (1951) tidal prism flushing model as they would exist under the mean annual freshwater inflow rate of 305 $m^3 \cdot s^{-1}$.

TABLE 4. Observed salinity averages and freshwater fractions for box segments of the Miramichi Estuary as compared with predicted salinity derived from Ketchum's tidal prism flushing model. Comparative data are compiled from each of four seasonal monitoring periods. FW = freshwater input from drainage basin.

Station (Fig. 3)	Observed salinity (‰)	Freshwater fraction	Salinity (‰)	Predicted freshwater fraction	Box model segment (Fig. 3)
		February 1977 (FW = 60 ± 2 $m^3 \cdot s^{-1}$)			
			0.0	1.00	0
			12.0	0.57	1
			14.8	0.47	2
			16.2	0.42	3
			18.8	0.33	4
			22.1	0.21	5
2	9.5	0.66	24.4	0.13	6
4	17.4	0.38	23.8	0.15	7
			25.2	0.10	8
			24.9	0.11	9
8	24.0	0.14	24.6	0.12	10
9	26.1	0.07	26.0	0.07	11
			26.3	0.06	12
6, 7	27.7	0.07	26.9	0.03	13
		October 1976 (FW = 140 ± 30 $m^3 \cdot s^{-1}$)			
			0.0	1.00	0
			6.7	0.76	1
1	0.4	0.99	14.6	0.48	2
2	13.4	0.52	14.6	0.48	3
3, 4	18.5	0.34	15.4	0.45	4
			21.3	0.24	5
			21.6	0.23	6
12	22.8	0.19	22.7	0.19	7
			23.2	0.17	8
			23.8	0.15	9
			24.9	0.11	10
		February 1976 (FW = 240 ± 20 $m^3 \cdot s^{-1}$)			
			0.0	1.00	0
			4.8	0.83	1
			6.4	0.77	2
			10.1	0.64	3
4	12.1	0.57	14.8	0.47	4
18	13.9	0.50	17.9	0.36	5
12, 8, 5	16.7	0.41	20.2	0.28	6
9	18.2	0.35	20.7	0.26	7
			21.0	0.25	8
6, 7, 17	25.0	0.11	23.8	0.15	9
		May 1976 (FW = 1000 ± 200 $m^3 \cdot s^{-1}$)			
1, 2	2.6	0.91	0.0	1.00	0
3, 4	7.6	0.73	1.1	0.96	1
			1.1	0.96	2
			5.0	0.82	3
			12.0	0.57	4

example, the negative SPM observed in the centre of the Inner Bay during some observation periods indicates that net deposition may have taken place over the mud facies identified by Reinson (1976). Such deposition of SPM seaward of a confined channel flow from an estuary has occurred in other estuaries (Allen et al. 1980) and has been expected to occur in the Miramichi (Krank 1981; Winters 1981, 1983). The apparent excess of suspended sediment during October 1976 is probably due to resuspension of bottom sediments that was noted to occur at the time of sampling, when winds across the shallow bay created 1.0-m-high waves.

The negative ΔC results for trace metals Zn, Cu, Pb, and Cd suggest that a mechanism exists for the removal of significant proportions (up to 70%) of the labile metal from the water under all freshwater inflow conditions. Removal of Pb occurs predominately in the upper and middle portions of the river

TABLE 5. Observed water quality concentration factors (C_f) as a function of river input concentrations in the Miramichi Estuary. Concentration factors are given for each box segment of the Ketchum tidal prism flushing model for which seasonal monitoring data were available. FW signifies freshwater input from the drainage basin.

Box model segment (Fig. 3)	Observation station (Fig. 3)	Freshwater fraction	SPM	POC	Fe	Mn	Zn	Cu	Pb	Cd
			February 1977 (FW = 60 ± 2 $m^3 \cdot s^{-1}$) at river input concentrations ($\mu g \cdot L^{-1}$) of:							
			5513	*380*	*106*	*106*	*3.24*	*0.39*	*1.4*	*0.053*
6	2	0.66	2.73	3.96	1.24	0.53	0.93	1.35	1.00	0.52
7	4	0.38	0.63	1.30	0.40	0.36	1.03	0.77	0.11	0.30
10	8	0.14	0.04	0.35	0.06	0.11	0.59	0.55	0.02	0.36
11	9	0.07	0.42	0.62	0.26	0.09	0.55	0.60	0.02	0.60
13	6, 7	0.01	0.05	0.27	0.05	0.05	0.49	0.59	0.02	0.45
			October 1976 (FW = 150 ± 30 $m^3 \cdot s^{-1}$) at river input concentrations ($\mu g \cdot L^{-1}$) of:							
			4500	*387*	*84*	*44*	*3.23*	*0.76*	*2.00*	*0.072*
2	1	0.99	1.32	0.99	0.99	0.99	0.99	0.99	0.99	0.99
3	2	0.52	1.11	0.90	0.60	0.84	1.05	0.88	0.21	0.88
4	4	0.34	1.17	0.92	0.40	0.46	0.51	1.80	0.06	0.72
7	12	0.19	1.50	0.68	0.05	0.09	0.34	0.57	0.01	0.47
			February 1976 (FW = 240 ± 20 $m^3 \cdot s^{-1}$) at river input concentrations ($\mu g \cdot L^{-1}$) of:							
			1161	*388*	*45*	*24*	*6.30*	*0.64*		
4	4	0.57	4.19		0.98	0.68	0.67	0.56		
5	18	0.50	1.71	0.78	0.70	0.83	0.44	0.39		
6	5, 8, 12	0.41	0.82	0.85	0.74	0.94	0.50	0.38		
7	9	0.35	0.89		0.29	0.62	0.36	0.27		
9	6, 7, 17	0.11	0.73	0.55	0.30	0.43	0.37	0.27		
			May 1976 (FW = 1000 ± 200 $m^3 \cdot s^{-1}$) at river input concentrations ($\mu g \cdot L^{-1}$) of:							
			23 900	*2810*	*137*	*24*	*5.30*	*1.31*	*0.170*	*0.062*
0	1	0.91	1.02	1.20	1.16	1.27	0.99	1.17	0.85	2.61
0	2	0.77	0.85	1.15	1.07	1.48	0.57	0.69	7.97	0.38
1	3	0.81	0.61	0.99	0.89	1.23	0.64	0.80	0.38	0.60
1	4	0.49	0.54	0.76	0.77	0.75	0.64	0.55	0.62	0.95

estuary but Zn and Cu removal appears to be more common in areas of the western and central Inner Bay, except during very high river inflow conditions when Zn and Cu removal appears to take place in the river estuary. Cadmium removal appears to occur only in the river estuary, apparently under a variety of freshwater conditions.

Metal is also transported through the estuary in the particulate form as part of the total SPM. Although some of the metal in the SPM is unreactive in normal aqueous environments, some fractions associated with surface coatings on mineral grains or complexed with associated organics may be potentially reactive. Due to the small quantities available for analyses, the SPM samples could not be tested for leach reactions as Willey and Fitzgerald (1980) had done on bottom sediments from the Miramichi. In their analyses of fine-grained bottom sediments they found that about 7% of the total Fe was leachable with weak acetic acid (pH 2.1) and that 45% of the total Mn and 34% of the total Zn was weak acid leachable. These percentages of leachable metal in bottom sediments appear to be about 15% lower than those found for analyses of SPM in the St. Lawrence River (P. A. Yeats, B.I.O., Dartmouth, N.S., personal communication). In our analyses we were only able to determine total metal content of the SPM, and these analyses were reliably limited to determinations of Fe, Mn, and Zn (Table 7).

Flushing Rates of Water Quality Parameters

Observed concentration data obtained from each monitoring station were converted to average concentrations for each appropriate box in the Ketchum model. Because the estuary is not well mixed and most of the parameters we wish to model do not behave conservatively we have developed a conversion factor for each box segment average concentration. This factor is a ratio of $\bar{C} - C_0 (1 - \mathrm{FW}_f)$ to $C_r \times \mathrm{FW}_k$, where FW_k is the freshwater fraction determined from the Ketchum model (Table 4). All other symbols in this ratio are as previously defined. This conversion factor is then multiplied by the product of C_r and FW to give the mass transfer through any box at an assumed quasi-steady-state flow determined by FW. When C_r is multiplied by 10^{-6} and the product of the first and second terms is multiplied by 86.4×10^3 the flushing rate is given as kilograms per day (Table 8). For two of the seasonal monitoring periods, October 1976 and May

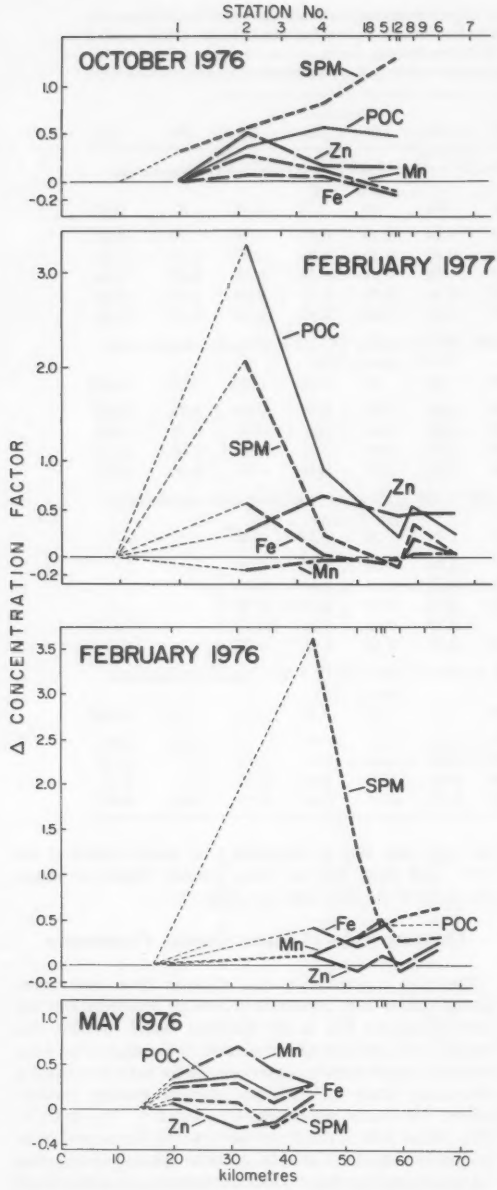

FIG. 5. Variation in the concentration factor of various water quality parameters with respect to the observed freshwater fraction at each monitoring station through the Miramichi Estuary. The Δ concentration factor is determined as the difference between the mean concentration factor, $\bar{C}_f$, and the freshwater fraction, FW_f, and therefore depicts the departure from conservative mixing in the estuary.

1976, no observations of water quality were made at the mouth of the Inner Bay. To complete the predictions for flushing rates for these periods we note that the lines of observed salinity and predicted salinity, or FW_f and FW_k, converge in the Inner Bay. We have thus used the relationships established with FW_k and C_r to derive predicted values of $\bar{C}$ for the last box in the Ketchum model. After establishing these values the flushing rates were calculated as with all other observed data. The predicted flushing rates based on predicted concentrations are shown in Table 8 in parentheses.

The flushing rates of SPM and POC from the river during periods of low to moderate river flow are always lower than the flushing rates of these materials leaving the river estuary (through station 4). The flushing rates of SPM and POC during the spring flood period are much higher, and at that time of year a greater mass of material enters the river estuary than is flushed out. The excess SPM retained in the river estuary is approximately 10^6 kg·d^{-1}. The apparent flushing of the Inner Bay is highly variable with each season and river flow condition. Much of this variation is probably related to factors that have not been quantitatively considered in our model calculations, such as resuspension of bottom sediments by flood currents or wave activity. Under winter ice, there is a net deposition of SPM which produces a negative flushing rate in February 1977 and February 1976. The net difference between SPM flushing rates from the river estuary as compared with the Inner Bay, during the spring flood, suggests that 124×10^3 kg SPM·d^{-1} is retained in the Inner Bay.

An exception to the SPM trend occurs in the data from October 1976 when there is an indication that slightly more Fe, Zn, and Pb enter the river estuary than is flushed out (Table 8). During the spring flood all labile metals appear to be accumulating in the river estuary.

Vilks and Krauel (1981) compiled mean monthly freshwater input data for a 10-yr period ending in 1976 (Fig. 6). From these data they compiled cumulative probable ranges (20–80%) of discharge rates for each month. Superimposed on this plot is the range of FW's observed in 1976 and 1977 when the geochemical sampling programs for this work were carried out. Using the 50% probability plot for FW's and the extremes of 20–80% cumulative probability we have estimated the probable number of days in a year that each of the sampling periods represents. The estimations are as follows: 14 d at FW = 60 ± 2 m^3·s^{-1}; 211 d at FW = 150 ± 30 m^3·s^{-1}; 101 d at FW = 240 ± 20 m^3·s^{-1}; 39 d at FW = 1000 ± 200 m^3·s^{-1}. The number of days in an average year was then multiplied by the daily flushing rate for each water quality parameter, as compiled in Table 8, to give the annual transport rates in Table 9.

The annual transport of each water quality parameter has been computed for principal segments of the Miramichi system: the river input, between the lower end of the river estuary, and the Inner Bay and the seaward end of the Inner Bay. From these data we are able to compare the gain or loss of transported water quality constituent between the river and the mouth of the estuary. The decreased quantities of transported SPM between the river inputs and the mouth of the estuary indicate that the system is a sink for some sediments, with 1700 t being deposited in the river estuary and 23 150 t being deposited in the Inner Bay annually.

TABLE 6. Concentration of water quality parameters (SPM, POC, and labile metals) after subtra
and predicted losses due to mixing between river water and salt water in the estuary, $C_r \times FW_f$. R
the estuary, and a negative value signifies sedimentation or precipitation within the estuary. ΔC_{ss}

Box model segment	Observation station	SPM (C_0 = 1000)	POC (C_0 = 60)	Fe (C_0 = 3.0)	Mn (C_0 = 1.1)	(C_0
					February 1977 (FW = 6	
6	2	10 971	1228	60	−14.2	
7	4	758	312	1	−2.8	
10	8	−1 111	28	−10	−4.1	
11	9	1 000	153	18	1.1	
13	6, 7	−770	39	1	3.2	
					October 1976 (FW = 15	
2	1	1 475	0.0	0.0	0.0	
3	2	2 205	118	6.7	13.6	
4	4	3 075	185	5.0	4.6	
7	12	5 085	141	−11.8	−5.3	
					February 1976 (FW = 24	
4	4	3 773		18	2.2	
5	18	905	79	9	7.4	
6	5, 8, 12	−114	135	14.8	12.0	
7	9	−23		−2.8	5.8	
9	6, 7, 17	−170	117	8.5	6.7	
					May 1976 (FW = 1000	
0	1	2 539	810	34	8.5	
	2	1 682	1054	41	16.8	
1	3	−4 970	494	11	9.9	
	4	685	728	38	5.7	

fter subtracting fractions contributed from seawater end member, C_0, × FW_f. Residual concentration signifies "contamination" from within ary. $\Delta C_{\mu g \cdot L^{-1}} = \bar{C} - [C_0 \times (1 - FW_f)] - (C_r \times FW_f)$.

	Zn (C_0 = 0.89)	Cu (C_0 = 0.1)	Pb (C_0 = 0.01)	Cd (C_0 = 0.025)
(FW = 60 ± 2 $m^3 \cdot s^{-1}$)				
	0.48	0.23	0.61	−0.02
	1.55	0.09	−0.38	−0.02
	0.69	0.07	−0.18	−0.01
	0.73	0.11	−0.08	0.0
	0.67	0.13	0.0	0.0
FW = 150 ± 30 $m^3 \cdot s^{-1}$)				
	−0.01	0.0	0.0	−0.02
	1.29	0.23	−0.63	0.01
	−0.04	1.04	−0.57	0.01
	−0.24	0.21	−0.37	0.0
FW = 240 ± 20 $m^3 \cdot s^{-1}$)				
	0.25	−0.04		
	−0.82	−0.12		
	0.04	−0.08		
	−0.52	−0.12		
	0.85	0.01		
= 1000 ± 200 $m^3 \cdot s^{-1}$)				
	0.34	0.33	−0.01	0.10
	−1.27	−0.13	1.22	−0.03
	−1.07	−0.03	−0.08	−0.02
	0.34	0.03	0.02	0.02

TABLE 7. Concentration of particulate Fe, Mn, and Zn (micrograms per litre) in the water sample. The percentage particulate metal of the whole metal concentration (particulate plus total labile metal) is shown in parentheses.

Box model segment	Observation station	Fe	Mn	Zn
		February 1977		
6	2	570(81)	16(22)	2.9(52)
7	4	117(74)	6.2(14)	0.75(21)
11	9	48(66)	2.6(22)	0.17(15)
		October 1976		
2	1	271(76)	20(31)	4.90(60)
3	2	179(78)	21(36)	1.24(29)
4	4	166(83)	22(52)	1.37(56)
7	12	202(99)	20(86)	3.43(90)
		February 1976		
4	4	180(80)	3.15(16)	1.42(27)
		May 1976		
0	1	1073(87)	29(49)	3.19(38)
	2	778(84)	17(32)	7.43(72)
1	3	653(84)	10(25)	3.60(52)
	4	542(83)	11(39)	4.36(59)

About 46% of the annual export of SPM from the river estuary to the Inner Bay occurs during the 39 d of spring flood. The estimated 93 900 t of SPM exported from the river estuary is in close agreement with the 90 000 – 110 000 t calculated by Winters (1981, 1983) who used a model that considered tidal inequalities and two-way transport of SPM through the section.

The calculated annual transport of Fe, Mn, Zn, and Cu indicates that more labile metal is exported from the system than enters the system from the river. There are two possible explanations for these results: (1) these metals could be entering the river estuary from sources along the estuary, such as industrial effluents, or (2) metal could be released to solution from the SPM and bottom sediments.

Geochemical Interactive Model

In the previous sections we have dealt mainly with the transport of total SPM and labile trace metals. We will now consider the particulate metal carried in the SPM, and discussion will focus on possible interactions between the SPM and labile metals and between the bottom sediments and the metals transported in the water mass. Interactive models (Fig. 7) are proposed for Fe, Mn, and Zn to demonstrate feasible sinks and sources of metal throughout the Miramichi Estuary system.

IRON

The amount of total particulate Fe transported into the Miramichi Estuary each year is 4200 t. Less than half of this amount of particulate Fe is exported from the system. The concentration of Fe in the SPM decreases from 4.39% in the river to 2.85% in the exported SPM (Table 10). From results of analyses of fine-grained surficial bottom sediments, Willey and Fitzgerald (1980) have found that the fraction of reactive metal (weak acid leachable and oxidizable) also changes in each of the subenvironments of the Miramichi system. They found the reactive percentages of total Fe to be 17.6% in the river, 22.5% in the estuary, and 13.2% in the Inner Bay. We have applied these results to our particulate metal transport data to give some indication of the potential reactive metal in the SPM. Because of the degree of resuspension of fine-grained bottom sediments it is expected that the percentage of reactive metal in SPM will be similar to the bottom sediments. The computed transports of reactive and residual Fe in the SPM show that the absolute quantities of both fractions decrease in passing from the river to the export from the system.

The losses of particulate metal due to deposition within each major segment of the Miramichi have been calculated. With 1700 t of SPM being deposited in the river estuary we assume that 4.39% of this material will be Fe (75 t), and with 23 900 t of SPM being deposited in the Inner Bay at 4.01% Fe, a loss of 928 t of particulate Fe occurs in the Inner Bay.

The actual losses of particulate Fe from the SPM have been estimated by determining the differences in input and output concentrations through each segment. For example, after subtracting the 75 t of Fe lost through sedimentation in the river estuary, we calculate that 4126 t would remain as a total particulate load. However, the export of 93 900 t of SPM at an average concentration of 4.01% particulate Fe means that only 3765 t of Fe is transported out of the river estuary into the Inner Bay. This means that further loss of 357 t of particulate Fe must have occurred in the transport through the river estuary. We have schematically shown this loss to be initially to the dissolved phase (Fig. 7a), but then there would have to be an even greater precipitation of labile metal in the river estuary in order that the exported quantity of labile metal could be reduced to 770 t at the exit from the river estuary. There is in fact a short-term increase in labile Fe in the river estuary, as noted in Fig. 5. A similar analysis can be carried out for the Inner Bay segment to show that of the total input of 3765 t of particulate Fe, 928 t is deposited directly with the SPM sedimentation. A further 821 t of Fe is lost to solution or by precipitation, as indicated by the decrease in concentration of Fe in the 70 750 t of SPM transported through the Inner Bay (4.01% input, 2.85% output). In the Inner Bay segment we have indicated that some of the particulate Fe could be converted to labile Fe to bring the exported total labile Fe up to 980 t.

If our simple model of deposition and precipitation is correct then there is an appreciable sink of Fe in the bottom sediments of the Miramichi system. In the river estuary there is approximately 10.5 km^2 of mud bottom sediments in a total area of 28.5 km^2. If we assume that initially these mud sediments contained the same concentration of Fe as the river bottom sediments (2.28%), and that the addition of Fe from the SPM and from adsorption and precipitation from the water column was responsible for increasing the bottom sediment concentration to 2.72%, then an addition of 327 t of Fe would be required to proportionately increase the Fe concentration in a layer of mud 0.5 cm thick (assuming the density of mud to be 1.39 $g \cdot cm^{-3}$ with a water content of 70%).

In the Inner Bay segment the annual deposition of particu-

TABLE 8. Flushing rates of SPM, POC, and labile metal from river, river estuary, and the total estuarine system. Calculations are based on observed concentrations in segments of the Ketchum tidal prism flushing model and assumed quasi-steady-state accumulation of water quality parameters at the seasonal freshwater inflow rates shown by FW. Values in parentheses are predicted flushing rates based on predicted concentrations. Flushing rate $F_{kg \cdot d^{-1}} = 86.4 \times 10^{-3}\ FW[\bar{C} - C_0\ (1 - FW_f)]/FW_k$.

	SPM	POC	Fe	Mn	Zn	Cu	Pb	Cd
				February 1977				
River	28 500	2 000	500	550	16	2.0	7.3	0.3
River estuary	120 100	15 550	1 380	1300	95	8.2	5.2	0.003
Inner Bay	−124 400	7 430	350	700	121	22.5	3.5	0.2
				October 1976				
River	58 300	5 000	1 100	570	42	9.5	26.0	1.0
River estuary	137 400	9 160	950	570	30	37.2	3.1	1.0
Inner Bay	(160 400)	(9 400)	(2 600)	(900)	(58)	(17.2)	(3.6)	(0.9)
				February 1976				
River	24 100	8 040	950	500	130	13.0		
River estuary	197 000		1 900	700	173	13.8		
Inner Bay	−50	240	1 560	1300	207	10.4		
				May 1976				
River	2 065 000	242 800	11 840	2070	460	112	15.0	5.4
River estuary	1 115 400	189 200	9 330	1560	270	60	8.6	4.1
Inner Bay	(991 000)	(208 800)	(6 980)	(1330)	(403)	(91)	(1.6)	(0.9)

late Fe with the 29 150 t of SPM at a concentration of 4.01% Fe would be 928 t. A further 611 t of Fe has been calculated to be deposited from direct precipitation or adsorption on the bottom sediments. If we again assume an initial bottom sediment concentration of 2.28% Fe over the area of mud deposition in the Inner Bay (114.8 km^2) but an annual incremental depth of only 0.1 cm then the initial mass of Fe in the bottom sediment layer can be calculated to be 3400 t. With the addition of a total of 1539 t the average concentration of Fe in the bottom sediments would become 3.29%. The observed average concentration of Fe in the mud in the Inner Bay is 3.35%.

MANGANESE

Using the same procedure for calculations of particulate Mn transport, as was followed with Fe, we note several opposite trends in the apparent geochemical interactions (Fig. 7b). The net export of both labile and particulate Mn from the estuary is greater than the input from the river. This suggests significant additions of Mn from sources located in the estuary.

The obvious contrasts with particulate Fe are that the concentration of Mn in the SPM is much higher than the concentration of Mn in the bottom sediments (Table 10), and the SPM concentration increases in going from the river (0.144%) to the river estuary segment (0.222%) to the exported SPM from the Inner Bay (0.312%). Unlike Fe, the Mn content in bottom sediments decreases seaward, decreasing from 0.070% in the river sediments to 0.040% in the fine muds of the Inner Bay. Another contrast with particulate Fe is that much more of the particulate Mn appears to be potentially reactive, ranging from 96% of the total particulate Mn in the river sediments to 89% in the river estuary sediments to 77.3% of the particulate Mn in the Inner Bay sediments.

Only 2 t of particulate Mn appears to be deposited with the SPM in the river estuary. The remaining 136 t of particulate Mn must be augmented by an additional 72 t of particulate Mn to reach the level of 208 t exported from the river estuary. A relatively small addition of 10 t must also be added to the labile Mn to reach the 270 t exported from the river estuary segment.

Using the same logic employed with the Fe interactions with bottom sediments we find that the potential release of Mn from the 0.5-cm-thick bottom mud facies would only yield about 19 t. This calculation is based on the assumption that 0.7 t would be mobilized from the freshly deposited SPM and a further 18.2 t could be released from bottom sediments as they adjust to the difference between river concentrations of 0.070% to 0.042% in the river estuary. This raises a question as to the source of the additional 64 t of Mn. Possibly, some of this additional metal is obtained from leaching of Mn from sediments buried below the 0.5-cm surface layer. In the data compiled by Winters et al. (1978) we found that the average concentration of Mn at depths below 5 cm in the cored sediments reached 0.03%. It is quite possible that some of the metal released from buried sediments diffuses back to the surface, as Sundby et al. (1981) have suggested for the St. Lawrence Estuary. The flux of this Mn could then be added to resuspended bottom sediments or could enter the water column as labile metal. The flux from a 0.5-cm-thick layer under the entire river estuary bottom would be 43 t·yr^{-1} to give a total of 62 t. This would still be approximately 20 t less than is required to balance the model for the river estuary segment. The only remaining likely source is injections of Mn from the pulp mill effluents, probably in association with the high loadings of POC.

When we examine the interactions of Mn in the Inner Bay segment we see that 51 t of Mn is probably deposited with the 23 150 t of SPM settled in the Inner Bay. The remaining 157 t of particulate Mn transported through the Inner Bay would have to be supplemented by an additional 64 t of

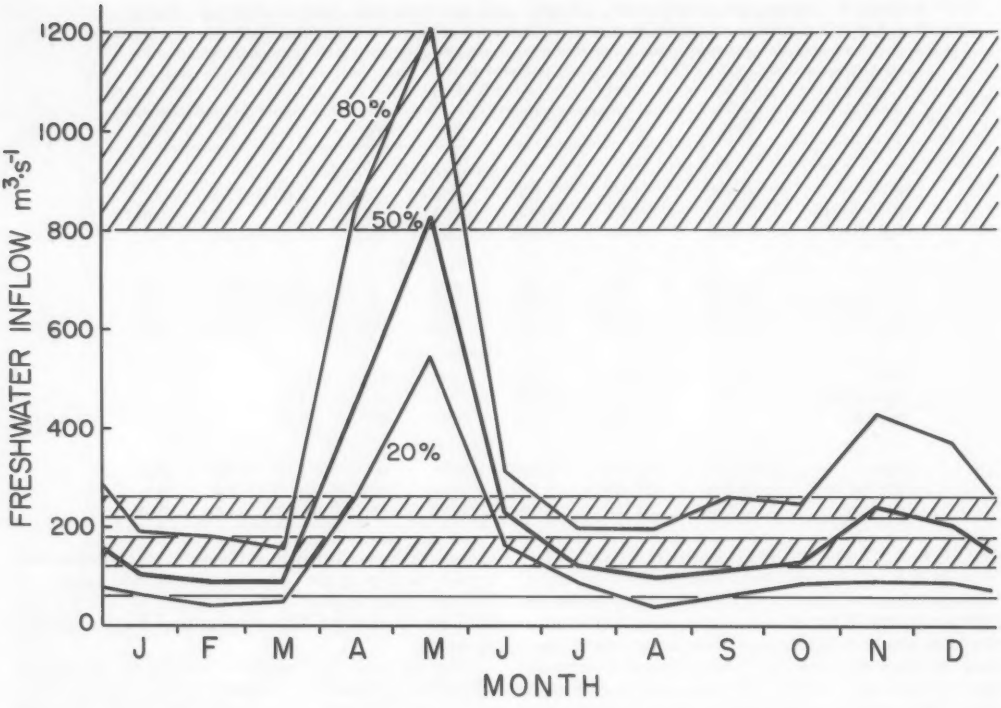

FIG. 6. Cumulative probability plot of monthly freshwater inflow rates after Vilks and Krauel (1981) based on 10-yr averages. Horizontal cross-hatched areas represent range of freshwater inflow rates included in observation periods for the geochemical transport study of this paper.

particulate Mn to reach the final export sum of 220 t. The labile metal export also increases to 380 t, so there would have to be 110 t of Mn added to this phase of the annual transport. If we again consider the bottom sediments as a possible source for this metal we find that the 23 150 t of freshly deposited SPM might remobilize 42 t of Mn and that a layer of mud 0.3 cm thick could release an additional 108 t of Mn. This total reflux of 150 t would still require about 24 t of Mn. Some of this metal may be derived from diffusion of metal from deeper layers in the sediment. In any case, it appears that a significant quantity of Mn may be available for remobilization from the bottom sediments.

ZINC

The interactive model for Zn is similar to both of the previous models presented for Fe and Mn. In the river estuary, Zn behaves like Fe in that there appears to be annual losses of Zn from the labile transport and reductions of the particulate transports as well (Fig. 7c). We consider that some of this loss may be by adsorption on bottom sediments or by direct precipitation. The budget for a bottom sediment sink for Zn is not as convincing as could be argued for Fe. Although the concentration of Zn in the bottom mud of the river estuary is greater as compared with Inner Bay, the river bottom sediments contain an even greater concentration. The relatively small addition of 16 t of Zn to the bottom muds is too little to be accurately identified in our analytical mean concentration. The required flux of Zn out of the bottom sediments in the Inner Bay is 34 t. If we again assume that this can be obtained from a thin surface layer of mud about 0.2 cm thick the depletion yield would be 38 t. Approximately 56% of this additional Zn appears to be added to the SPM particulate metal transported out of the Inner Bay. The reactive portion of particulate Zn varies from 60% in the river to 82% in the river estuary to 58% in the Inner Bay.

COPPER

We were not able to determine the concentration of particulate Cu in the SPM because of detection limits in the generally small samples and therefore could not complete an interactive model for this metal. However, there is an increase in the transport of labile Cu out of the river estuary and the Inner Bay as compared with the transports into the system from the river. Bottom sediment concentrations remain nearly constant

TABLE 9. Annual transport (tonnes) of water qualities through threshold segments of the Miramichi system transports are calculated from daily transport rates (Table 8) proportioned to the estimated probable mean monthly freshwater inputs (see Fig. 7). — indicates that no observations were made for FW = 240 $m^3 \cdot s^{-1}$, so annual transports could not be calculated for POC, Pb, and Cd.

	SPM	POC	Fe	Mn	Zn	Cu	Pb	Cd
River	95 600	11 360	800	260	40	7.7	6.1	0.43
River estuary	93 000	—	770	270	35	11.7	—	—
Inner Bay	70 750	10 250	980	380	50	8.5	—	—

throughout the estuary, and therefore, the trend may not be the same as that observed for Zn. There may, however, be a similar interactive model for these two metals.

LEAD

Because of lack of a complete set of seasonal observations for labile Pb and no analyses of Pb in the SPM we can only speculate as to the approximate transports of this metal through the system. Using the available data on labile Pb through the segments of the Miramichi it appears that 1.0 t or less of Pb may be transported out of the river estuary and the Inner Bay each year. This would suggest that the river estuary bottom sediments may be a significant sink for Pb, perhaps as much as 5 t each year. There is only a slight, and perhaps insignificant gradient, in Pb concentration in the bottom sediments in passing from the river estuary to the Inner Bay. Analyses of particulate Pb in the SPM would be required to determine the importance of this transport phase.

CADMIUM

Lack of complete data sets for Cd also prevent us from making firm statements as to the interaction of this metal with the SPM or bottom sediments. As was the case with Pb, we have noted marked decreases in labile Cd in the waters of the outer river estuary and Inner Bay. This would suggest a possible sink for this metal in the sediments of the river estuary. This possibility may be somewhat confirmed by the analyses of a standard sample of mud we obtained from the river estuary which contained 0.6 $\mu g\ Cd \cdot g^{-1}$, which is about two or three times the concentration we found in a similar mud from the Bay of Chaleur.

Environmental Implications

Our examination of the flushing characteristics of the Miramichi Estuary and the geochemical interaction of metals has been based on an integration of transports over a year. Our data base for concentration of particulate and dissolved metals and our calculated daily flushing rates (Table 8) demonstrate the great importance of the spring flood period to the overall yearly flux of SPM and metals from compartments of the Miramichi system. Many studies of other estuarine systems have been based on short periods of observation during only one or two stages in the annual hydrologic cycle, so it is quite possible that similar estuaries may be described in quite different ways.

In the case of the Miramichi system 84% of the total annual input of SPM from the river occurs during the 39-d spring flood. About 45% of this SPM is then deposited in the river estuary during the flood period, and 55% of the annual export of SPM from the entire system also occurs at this time of the year. If we had considered the spring flood period as being representative of the dynamics of the Miramichi system over the whole year we would have concluded that the upper estuary was a sink for SPM and much of the particulate metal. Much of the spring-deposited SPM is resuspended during the rest of the year, and most of it is transported out of the river estuary. These annual processes provide ample opportunity for redistribution of particulate and labile metal, as suggested by several studies, cited below, of other estuaries.

There is general agreement that Fe is lost from both the dissolved and particulate phase in upper estuarine environments, as exemplified by the studies of Bewers and Yeats (1978, 1979) and Smith and Milne (1979). These processes are emphasized in the Miramichi Estuary during the spring flood period when, although 58% of the annual supply of labile Fe enters the river estuary, 21% of this input remains in the river estuary. Coupled with this loss of labile Fe is the calculated deposition of 1600 t of particulate Fe with the SPM. This amount of direct deposition of particulate Fe is 22 times the annual deposition; therefore, much of this material must be subsequently resuspended. The great amount of temporary deposition, adsorption, and precipitation must have a significant effect on removal of other trace metals at this time of year. The net spring export of all other labile metals (Mn, Zn, Cu, Pb, and Cd) is less than the inputs from the river, in spite of the fact that one-third to one-half of the annual river input occurs in the spring. Some of these metals may be reduced to relatively insoluble sulfides in the bottom sediments of the estuary, as suggested by Elderfield and Hepworth (1975). Manganese and Cd may be least affected by such an immobilization, as suggested by the fact that even during the spring flood 75% of the input labile Mn and 80% of the Cd is exported from the river estuary, whereas 58% of the labile Zn, 52% of the labile Cu, and 55% of the Pb are exported.

Much has been written about the cycling of Mn in estuarine systems. A common observation is that dissolved Mn concentrations are greater than would be predicted by conservative mixing in the upper estuary environment (Evans et al. 1977; Duinker et al. 1979; Morris et al. 1981). Some researchers have observed an enrichment of particulate Mn on SPM in various sections of estuaries (Evans et al. 1977; Yeats et al. 1979; Morris et al. 1981). These authors suggested that the source of elevated concentrations of dissolved Mn is dissolution of reduced Mn from near-surface bottom sediments

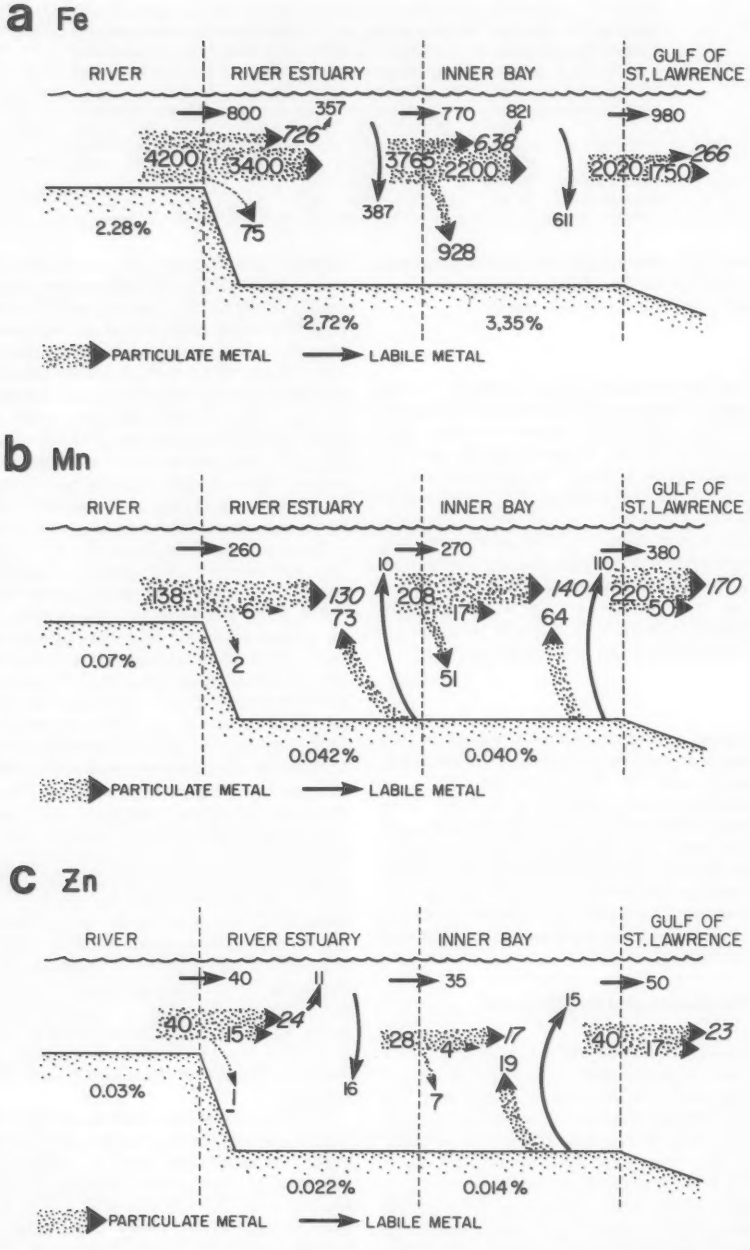

FIG. 7. Interactive schematic model of particulate and labile metals in the Miramichi Estuary. Transports are in tonnes per year. Concentration of metals in fine-grained bottom muds are shown as percentages. Italicized numbers in particulate metal transport represent tonnes of potential reactive metal.

TABLE 10. Concentrations of total metal Fe, Mn, and Zn in SPM compared with concentrations of total Fe, Mn, Zn, Cu, and Pb in bottom sediments. Average percentages are compiled for principal segments of the Miramichi system. Concentration data for bottom sediments were taken from Willey and Fitzgerald (1980).

		SPM	Bottom sediments
River	Fe	4.39	2.28
	Mn	0.1439	0.0695
	Zn	0.0418	0.0282
	Cu		0.0032
	Pb		0.0200
River estuary	Fe	4.01	2.72
	Mn	0.2219	0.0417
	Zn	0.0297	0.0219
	Cu		0.0027
	Pb		0.0083
Inner Bay	Fe	2.85	3.35
	Mn	0.3115	0.0400
	Zn	0.0552	0.0138
	Cu		0.0029
	Pb		0.0080

with advection into the water column. Yeats et al. (1979) suggested that some of the excess dissolved Mn is precipitated in the water column to produce particles enriched in Mn. Under anoxic conditions in the Chesapeake Bay sediments, Eaton (1979) calculated that the flux of Mn out of these sediments accounts for four times as much metal entering the waters as could be obtained from the total annual input of both dissolved and particulate forms from the Susquehanna River. Eaton's flux rate of 20 $t \cdot yr^{-1} \cdot km^{-2}$ compares with our estimated flux of 1.5 $t \cdot yr^{-1} \cdot km^{-2}$ for Mn release from bottom muds of the Inner Bay of the Miramichi and 7.9 $t \cdot yr^{-1} \cdot km^{-2}$ for the muds from the river estuary bottom. Our estimated fluxes suggest that the river estuary muds are more reduced than the Inner Bay muds and could therefore also retain higher concentrations of insoluble metal sulfides.

Conclusions

In the Miramichi Estuary, water quality parameters such as total SPM and trace elements vary over a wide range of concentrations throughout the estuary. These variations are a function of freshwater inputs from the Miramichi River and the tidal prism flushing characteristics as well as geochemical interactions within the estuary. The observed concentration of labile Fe, Mn, Zn, and Cu exceeds the concentration that can be predicted by conservative mixing between the fresh and salt water in the river estuary segment of the system. The excess concentration of labile Fe is related to the turbidity maximum in the river estuary but the excess concentrations of Mn, Zn, and Cu are commonly seaward of the turbidity maximum.

Calculations of daily flushing rates based on the Ketchum tidal prism flushing model demonstrate that most of the SPM passes through the river estuary during most of the year when river inputs are low. During the spring floods the river input of SPM increases by nearly two orders of magnitude, and about half of this input is deposited in the river estuary.

The annual transport of labile metals through critical sections of the Miramichi Estuary demonstrates that more labile Fe, Mn, Zn, and Cu is exported from the system than enters from the river. The source of the excess Fe appears to be desorption from SPM. The excess Mn, Zn, and Cu is calculated to be from a thin surface layer (<0.5 cm) of bottom muds in both the river estuary and Inner Bay. The annual export of labile Pb and Cd is less than the input from the river, and it is therefore assumed that the river estuary bottom muds are the principal sink for these metals.

The export of particulate Fe is about twice as much as the labile Fe, but overall the estuarine system is a sink for both reactive and nonreactive Fe. By contrast, only about one-third of the total export of Mn is in the particulate form; however, there is a net increase in particulate Mn over the input from the river, and 75–80% of the particulate Mn is reactive. There are nearly equal amounts of labile and particulate Zn being exported from the Miramichi Estuary, and about 60% of the particulate Zn is reactive. There is no gain or loss of particulate Zn as compared with the river input.

During spring flood periods, which last for an average of 39 d, about 85% of the annual supply of SPM enters the river estuary from the Miramichi River. Also during this time, 30–55% of the annual supply of labile metals Fe, Mn, Zn, and Cu enters the system. Much of this spring influx of SPM and metal is temporarily stored in the river estuary but is eventually flushed into the Inner Bay, and eventually the labile metals are flushed out of the estuary over the rest of the year.

One of the important lessons learned from this study is that observations over an annual cycle are critical if we are to properly assess the annual flux from an estuary. Estimates of net annual flux may also be in error by as much as a factor of 2 if observations of quality concentrations are not made over properly representative sections of the estuary. These types of considerations are of special importance if the objective of a monitoring program is to establish the impact of pollution from a contaminated river or estuary.

Acknowledgments

Obviously, the collection of the very large number of samples and field data on which we have relied in this paper required the cooperation and dedication of many of our colleagues at the Atlantic Geoscience Centre. We are very grateful for the efforts of G. Vilks, G. Reinson, J. Willey, C. Schafer, K. Robertson, M. Gorveatt, R. Fitzgerald, R. Murphy, F. Jodrey, T. Cole, and D. Frobel, all of whom spent many uncomfortable days and nights in support of efforts to collect these data. We also thank Drs M. Bewers, R. Cranston, and J. Syvitski for reviewing earlier versions of this manuscript and making helpful suggestions for improving the text.

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Trace Element Distributions in the Gulf Stream Adjacent to the Southeastern Atlantic Continental Shelf — Influence of Atmospheric and Shelf Water Inputs[1]

GORDON T. WALLACE,[2] NAN DUDEK, RHONDA DULMAGE, AND ORMONDE MAHONEY

Skidaway Institute of Oceanography, P.O. Box 13687, Savannah, GA 31406, USA

WALLACE, G. T., N. DUDEK, R. DULMAGE, AND O. MAHONEY. 1983. Trace element distributions in the Gulf Stream adjacent to the southeastern Atlantic continental shelf — influence of atmospheric and shelf water inputs. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 183–191.

As part of an effort to define processes that control the exchange of trace elements between southeastern Atlantic shelf waters and the Gulf Stream at the shelf boundary we determined the vertical distribution of particulate Al, Fe, Mn, Ni, Cu, Zn, Pb, and Cd and total dissolvable Fe, Ni, Cu, Zn, Pb, and Cd in the Gulf Stream adjacent to the shelf. Simultaneous determination of the particulate forms of Cu, Ni, and Cd and potential carrier phase indicators such as particulate Al, Fe, Mn, and organic C permitted assessment of the relative importance of clay minerals, hydrous oxides, and organic matter in the control of the trace element content of suspended matter. Particulate trace element concentration data were used in conjunction with a first-order removal model to estimate downward vertical fluxes of Fe, Mn, Ni, Cu, Pb, and Cd. Comparison of these flux estimates with atmospheric inputs of these same elements indicated that, with the possible exceptions of Mn and Cu, vertical processes largely control the distribution of trace elements in the Gulf Stream and that these processes are primarily biological in nature. Estimates of "new" production, in concert with an estimated vertical flux of C and the observed nitrate concentration profile, were used to predict a vertical eddy diffusion coefficient of ~0.4 $cm^2 \cdot s^{-1}$ in the highly stratified region of the Gulf Stream. Injection of trace elements from shelf waters into surface Gulf Stream waters, with the possible exceptions of Mn and Cu, are apparently masked by a combination of atmospheric input and large-scale physical mixing processes.

WALLACE, G. T., N. DUDEK, R. DULMAGE, AND O. MAHONEY. 1983. Trace element distributions in the Gulf Stream adjacent to the southeastern Atlantic continental shelf — influence of atmospheric and shelf water inputs. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 183–191.

Dans le but de définir les processus réglant l'échange d'éléments en traces entre les eaux du plateau continental de l'Atlantique sud-est et le Gulf Stream à la limite du plateau, nous avons déterminé la distribution verticale de Al, Fe, Mn, Ni, Cu, Zn, Pb et Cd particulaires et de Fe, Ni, Cu, Zn, Pb et Cd solubilisables totaux dans le Gulf Stream au voisinage du plateau. Grâce à une détermination simultanée des formes particulaires de Cu, Ni et Cd, et d'indicateurs potentiels de la phase porteuse, tels que Al, Fe et Mn particulaires et C organique, il a été possible d'évaluer l'importance relative des minéraux de l'argile, des oxydes hydreux et de la matière organique dans le contrôle des quantités d'éléments en traces de la matière en suspension. Les données sur la concentration de ces éléments ont été utilisées de concert avec un modèle d'enlèvement de premier ordre pour estimer le transport vertical vers le bas de Fe, Mn, Ni, Cu, Pb et Cd. Une comparaison de ces estimations de flux avec les apports atmosphériques des mêmes éléments indique que, sauf peut-être pour Mn et Cu, les processus verticaux règlent en grande partie la distribution des éléments en traces dans le Gulf Stream et que ces processus sont avant tout de nature biologique. On a utilisé des estimations de production « nouvelle » en même temps qu'un flux vertical estimé de carbone et le profil de concentration des nitrates observé pour prédire un coefficient de diffusion tourbillonnaire verticale de ~0,4 $cm^2 \cdot s^{-1}$ dans la zone fortement stratifiée du Gulf Stream. Il semble que l'introduction d'éléments en traces en provenance des eaux du plateau dans

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Environmental Science Program, University of Massachusetts at Boston, Harbor Campus, Boston, MA 02125, USA.

Printed in Canada (J6860)
Imprimé au Canada (J6860)

les eaux superficielles du Gulf Stream, à l'exception possible de Mn et Cu, soit masquée par une combinaison d'apports atmosphériques et de processus de mélange physiques à grande échelle.

Received March 19, 1982
Accepted December 20, 1982

Reçu le 19 mars 1982
Accepté le 20 décembre 1982

PHYSICAL, chemical, and biological processes that control the horizontal and vertical distribution of metals in the oceans are still poorly understood. Vertical profiles of "dissolved" Cu, Zn, and Cd indicate that these elements are rapidly removed from the surface mixed layer (Bruland 1980 and references therein). Large-volume particulate samples (Bishop et al. 1977; Bishop et al. 1978; Bishop et al. 1980) and sediment trap collections (Wiebe et al. 1976; Honjo 1978; Spencer et al. 1978; Deuser and Ross 1980; Brewer et al. 1980; Deuser et al. 1981) support arguments for the rapid vertical transfer of particulate matter from oceanic surface layers on large particles which may include fecal material and/or large aggregates. It is clear that the distribution of metals which are depleted in the surface layers of the ocean are, in part, a function of their interaction with, and the subsequent transport by, particulate matter.

Despite the importance of adsorption and gravitational settling in removal of trace metals from oceanic surface layers, almost nothing is known of either the vertical distribution of particulate trace metals or the composition of suspended matter with which they are associated. Such data can be expected to provide insight into the nature of the processes that control trace metal distributions. Most suspended trace element concentration data available for oceanic regions are from surface samples (Wallace et al. 1977b and references therein; Krishnaswami and Sarin 1976). Buat-Menard and Chesselet (1979) reported geometric mean suspended trace metal data for deep waters (>300 m) of the tropical North Atlantic, while vertical profiles of particulate Mn from the Pacific (Landing and Bruland 1980; Klinkhammer and Bender 1980) and Atlantic (Bender et al. 1977) have been described. Most of these data are not accompanied by information on the nature of the suspended matter or concurrent soluble metal concentrations.

We report here the vertical profile of a number of trace elements at a single station in the Gulf Stream adjacent to the southeastern United States continental shelf (30°51.1′N, 79°41.8′W). Elements measured included particulate Al, Fe, Mn, Ni, Cu, Zn, Pb, and Cd, particulate organic C and N, and total dissolvable (pH ~2) Fe, Ni, Cu, Zn, Cd, and Pb.

Methods

SAMPLE COLLECTION

Samples were collected using 30-L teflon-coated General Oceanics GO-FLO bottles hung on Kevlar® line. The Kevlar® line was wound on a portable winch with a teflon-lined spool and guide. All "O" rings in the GO-FLO bottles were silicon rubber and all metal fittings on the exterior of the bottles were coated with epoxy paint, silicon rubber, or teflon. Each GO-FLO bottle was examined for metal chips generally found imbedded in the ends of bottles received directly from the factory. Previous experience indicated that some of these chips corrode readily and were probably steel; others appeared to be brass. Failure to remove these chips can lead to obvious consequences (see Fe results below).

Each GO-FLO bottle was dissassembled, meticulously cleaned with Micro® detergent, rinsed with deionized water, reassembled, totally immersed in 700 L of 6×10^{-4} mol $HCl \cdot L^{-1}$ in deionized water for 24 h, rinsed in deionized water, soaked in 700 L of deionized water for 48 h, rinsed with 1.2 mol $HCl \cdot L^{-1}$, followed by deionized water, and then leached with deionized water. All bottles were stored in plastic bags until used and then handled only with plastic gloves.

Once aboard ship, samples for particulate metal analysis were transferred on deck into precleaned 26-L polyethylene carboys for subsequent filtration. Samples for total dissolvable metals (metals solubilized at pH 2) were collected in three precleaned 500-mL conventional polyethylene bottles, acidified to ~pH 2 with Suprapur® HNO_3, and stored until analyzed. Following filtration, the Nuclepore® 0.4-μm, 47-mm-diameter filters, which had been preloaded into acid-cleaned polycarbonate filter holders on shore in a laminar flow clean bench, were transferred to small polyethylene vials in a small portable clean bench. Nuclepore® filters were acid cleaned before use as described by Wallace et al. (1977a) except that a 5-min sonication in 1.2 mol $HCl \cdot L^{-1}$ was incorporated into the procedure.

Polyethylene vials used to store the filters and polyethylene bottles used to store the total dissolvable metal samples were rigorously cleaned before use. After rinsing with acetone, 1.2 mol $HCl \cdot L^{-1}$, and deionized water, vials and bottles were immersed and filled, respectively, with 4 mol $HNO_3 \cdot L^{-1}$, sonicated for 3 h, rinsed and filled with deionized water, sonicated for 3 h, rinsed with quartz sub-boiling distilled ("Q") water, and finally filled with 1.2×10^{-2} mol Suprapur® $HCl \cdot L^{-1}$ in "Q" water.

Nutrient, chlorophyll, and particulate organic C and N samples (collected on precombusted Reeve Angel glass-fiber filters) were obtained immediately and frozen until analyzed. Salinity samples were also collected at each depth sampled. We were unable to measure temperature at our station but hydrographic data were obtained at stations near (<10 km) our station 3 d later (L. Atkinson, Skidaway Institute of Oceanography, Savannah, GA, personal communication) and in July 1978 (Atkinson et al. 1979).

SAMPLE ANALYSIS

Particulate trace metal, organic C, and N were analyzed as described by Wallace et al. (1977b). Chlorophyll concentrations were measured by the technique of Yentsch and Menzel

TABLE 1. Reagent blanks and spike recoveries.

Element	Reagent blank (nmol·L^{-1})	Blank SD (nmol·L^{-1})	Ambient seawater concentrations (nmol·L^{-1})	Spike concentrations added (nmol·L^{-1})	Recovery ±1 SD (%)
Cu	0.003–0.042	0.002–0.013	0.52–1.34	3.1–6.3	97±5
Zn	0.044–0.136	0.008–0.028	0.091–0.41	3.1–6.1	96±7
Ni	0.110–0.49	0.014–0.065	0.74–3.2	6.8–13.6	98±5
Cd	0.0026–0.0074	0.0009–0.0036	0.0024–0.042	0.178–0.36	94±3
Pb	0.0012–0.0058	0.0005–0.0039	0.048–0.075	0.097–0.193	95±5
Fe	0.81–1.32	0.021–0.25	0.64–4.5	14.3–28.6	102±5

(1963). Nitrate, phosphate, and silicate were measured with a Technicon autoanalyzer using the procedures of Glibert and Loder (1977).

A dithiocarbamate extraction technique similar to that described by Bruland et al. (1979) and Danielsson et al. (1978) was used to analyze total dissolvable Fe, Cu, Zn, Ni, Cd, and Pb. Preparation of the ammonium 1-pyrrolidinedithiocarbamate/diethylammonium diethyldithiocarbamate chelate solution and ammonium acetate buffer was as described by Bruland et al. (1979). One millilitre of preextracted chelate mixture and 2 mL of preextracted ammonium acetate buffer were added to a 250-mL acidified (pH ~2) seawater sample in a meticulously cleaned all-teflon sepratory funnel. The sample was shaken for 60 s, 5 mL of Freon (trichlorotrifluoroethane) (Burdick and Jackson Laboratories, Inc.) was added, and the sample was shaken for 180 s. After allowing 6 min for phase separation, the Freon extract was carefully drained into a preweighed 30-mL-capacity teflon vial. A second 5-mL portion of Freon was added and the extraction procedure repeated. The combined Freon extracts were examined for any carryover of seawater droplets, which if present were removed by micropipet. Following addition of 1 mL of 1.6 mol Suprapur®·L^{-1} or "Q" HNO_3 in "Q" water, the sample was placed on low heat on a hot plate and the Freon was slowly evaporated. After adjustment of the final weight with "Q" water, the aqueous extract was transferred to a 1.7-mL polyethylene vial and finally analyzed by flameless atomic absorption. Addition of the 1.6 mol "Q" HNO_3·L^{-1} to the Freon extract before evaporation was critical. When addition of 1.6 mol "Q" HNO_3·L^{-1} was made after evaporation of the Freon, low yields were observed. Acid digestion (1 mL of 16 mol "Q" HNO_3·L^{-1}) of the evaporated Freon extract did not improve the yield.

We did not find it necessary to redistill the Freon received from Burdick and Jackson based on analysis of its metal content before use. An added advantage of the use of Freon is the extremely low carryover of seawater in the Freon extract. If seawater droplets remaining in the Freon extract are removed, the resultant salt content of the final aqueous extract is so low that use of the deuterium arc for background correction could, in most cases, be omitted. Matrix effects, indicated by comparing the results of standard addition and standard comparator analyses of selected samples, were not observed. Nevertheless, background correction was generally used to preclude occasional erroneous signals from samples in which unnoticed carryover of salt might have occurred.

Total reagent blanks were obtained by repeating the entire extraction procedure with preextracted samples. Recovery of metals added to surface seawater collected from the western edge of the Gulf Stream was used to assess extraction efficiencies. The uncertainty in recovery values (Table 1) includes suitable propagation of errors in the determination of reagent blanks, ambient concentrations, and spiked seawater samples.

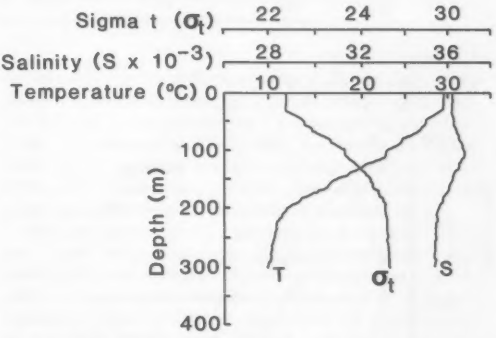

FIG. 1. Hydrographic data at 30°47.0′N, 79°46.0′W (<10 km from Gulf Stream station) taken 3 d after collection of trace element samples. (Hydrographic data collected by L. P. Atkinson under the Bureau of Land Management South Atlantic Outer Continental Shelf Program.)

Results

Hydrographic data taken 3 d later at a station <10 km away indicated the presence of a 30-m mixed layer with an intense pycnocline between 30 and 200 m (Fig. 1). These characteristics are typical of the Gulf Stream in this area in late summer (Hazelworth 1976).

Salient features of the vertical distribution of nitrate, chlorophyll, particulate Al, and particulate C (Table 2; Fig. 2) are a nutrient-depleted zone extending below the mixed layer, a deep chlorophyll maximum (DCM) at 100 m, a minimum in particulate Al concentration coincident with the DCM, and a rapid decline in particulate organic C below 100 m. The decline in particulate Al concentration from the surface to the minimum at 100 m was interpreted as a reflection of atmospheric input coupled with first-order removal from the upper 100 m (Wallace et al. 1981). The parameters controlling the increase in particulate Al with depth below 100 m are not known. Both transport from the adjacent shelf and/or

TABLE 2. Nutrient, chlorophyll, and mean particulate organic C (POC) ($n = 2$) concentrations in the Gulf Stream.

Depth	Nitrate ($\mu mol \cdot L^{-1}$)	Phosphate ($\mu mol \cdot L^{-1}$)	Silicate ($\mu mol \cdot L^{-1}$)	Chlorophyll ($\mu g \cdot L^{-1}$)	POC ± 1 SD ($\mu mol \cdot L^{-1}$)
30	0.10	0.01	1.36	0.03	1.72±0.05
60	0.09	0.04	1.48	0.04	2.2±0.01
100	1.02	0.06	1.17	0.23	1.7±0.1
160	6.2	0.31	2.23	0.02	0.63±0.22
245	10.6	0.53	3.46	0.01	0.37±0.03
286	14.9	0.81	5.85	0.01	0.37±0.07
390	21.9	1.33	10.94	0.01	0.35±0.07
433	25.4	1.49	13.3	0.02	0.42±0.16

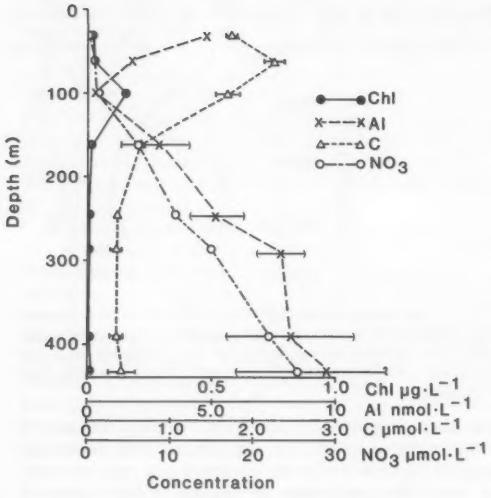

FIG. 2. Vertical profile of particulate Al, particulate organic C, nitrate, and chlorophyll. Error bars on C and Al values represent 1 SD. Where error bars are absent, the uncertainties lie within the dimensions of the symbols. (From Wallace et al. 1981.)

resuspension of Al from slope sediments are possible origins. We return to this question later when discussing vertical eddy diffusion in the Gulf Stream.

Concentrations of particulate Fe (Table 3) generally followed the profile of particulate Al. Excluding an anomolously high value at 100 m, the mean particulate Fe:Al ratio was 0.34 ± 0.09 mol·mol^{-1}. This value is close to the crustal ratio (0.33) (Taylor 1964). Several of the samples were apparently contaminated with Fe. These same samples were also contaminated with particulate Ni and particulate Cr. Examination of station records indicated that these samples were collected with the same GO-FLO bottle and suggested that not all metal chips (see Methods) had been successfully removed from the bottle before use.

Particulate Mn concentrations (Table 3) generally increased with depth, especially between 100 and 160 m. This rapid increase in concentration in near-surface waters is not unique and can also be seen in the data of P. Brewer reported in Klinkhammer and Bender (1980) and the data of Landing and Bruland (1980). Examination of this increase in the context of the particulate Al and particulate organic C profiles is of particular interest. The Mn:Al ratios of the shelfbreak particles (Table 4) were close to the crustal ratio of Taylor (1964) and 1−2 orders of magnitude lower than that observed in the Gulf Stream. Noncrustal Mn:C ratios in the surface 100 m were similar to those observed in Sargasso Sea surface waters (Wallace et al. 1977b) but increased dramatically in the 100- to 245-m depth interval in which the highest Mn:Al ratios were observed. High particulate Mn:Al ratios of suspended matter in the upper 500 m of the western Atlantic have also been observed by Chesselet et al. (1976).

Total dissolvable Cu concentrations (Table 5) were uniform with depth and similar in concentration to those recently measured in oligotrophic surface waters of the Pacific (Bruland 1980) and Atlantic (Moore 1978; Windom and Smith 1979; Boyle et al. 1981; Bruland and Franks 1983). Lack of correlation between total dissolvable Cu and nitrate reflects either a slower rate of release of Cu relative to that of nitrogen from settling particulate matter and/or the scavenging of Cu by settling particles (Boyle et al. 1977; Brewer et al. 1980).

Particulate Cu showed no significant trend with depth and ranged from 22 to 42 pmol·L^{-1} (Table 3). This range is similar to that observed in Sargasso Sea surface waters (30−37 pmol·L^{-1}) by Wallace et al. (1977b).

Total dissolvable Ni (Table 5) ranged from a low of 2.1 ± 0.2 nmol·L^{-1} near the surface to 5.3 ± 0.4 nmol·L^{-1} at 433 m. Recently determined concentrations of total dissolvable Ni in Sargasso Sea surface waters, 1.2−1.9 nmol·kg^{-1} (Boyle et al. 1981) and 2.3 nmol·kg^{-1} (Bruland and Franks 1983), are in close agreement with our surface values. Although there are few data points, the Ni concentrations we observed at 390−433 m are in reasonable agreement with those observed by Bruland and Franks (1983) in samples with similar nutrient concentrations. No significant trend with depth was noted in particulate Ni (Table 3) which ranged from 13 ± 3 to 27 ± 7 pmol·L^{-1}, concentrations similar to those observed for particulate Ni in Sargasso Sea surface waters (Wallace et al. 1977b).

The total dissolvable Cd profile (Table 5) is consistent with the earlier finding of Boyle et al. (1976), Martin et al. (1976), Bruland et al. (1978), Bruland (1980), and Bruland and Franks (1983). Surface concentration of Cd measured by Bruland and Franks (1983) in the Sargasso Sea was ~2 pmol·L^{-1}. Our surface concentration was less than

TABLE 3. Particulate trace metals in the Gulf Stream (values in parentheses = 1 SD).

Depth (m)	Al (nmol·L^{-1})	Fe (nmol·L^{-1})	Mn (nmol·L^{-1})	Ni (pmol·L^{-1})	Cu (pmol·L^{-1})	Zn (pmol·L^{-1})	Pb (pmol·L^{-1})	Cd (pmol·L^{-1})
30	4.7(0.4)	1.22(0.05)	0.067(0.007)	14(5)	33(9)	26(21)	19(3)	0.78(0.42)
60	1.74(0.04)	0.56(0.07)	0.133(0.005)	13(3)	28(6)	<11	7.9(0.4)	0.97(0.44)
100	0.33(0.15)	0.48(0.05)	0.107(0.015)	27(7)	22(2)	<11	10(2)	1.03(0.35)
160	3.0(1.3)	1.6(0.3)[a]	0.40(0.02)	104(34)[a]	42(3)	40(29)	11(1)	0.33(0.08)
245	5.2(1.5)	1.6(0.3)	0.44(0.09)	17(1)	25(9)	46(32)	6.7(0.6)	0.53(0.21)
286	7.8(1.5)	5.2(0.3)[a]	0.60(0.05)	298(9)[a]	25(2)	43(6)	23(1)	0.44(0.05)
390	8.2(2.6)	3.8(0.4)	0.51(0.14)	24(3)	30(5)	—[b]	20(1)	0.36(0.12)
433	9.6(3.7)	5.0(0.3)[a]	0.53(0.09)	150(22)[a]	30(6)	20(18)	25(2)	0.80(0.38)[a]

[a]Contamination suspected or evident.
[b]Relative SD > 1.

TABLE 4. Ratios of Mn to Al and C in the Gulf Stream and shelfbreak suspended matter.

Location	Depth (m)	Mn:Al (mol·mol^{-1})	Mn:C[a] (mol·mol^{-1})
Gulf Stream	30	1.4×10^{-2}	2.3×10^{-5}
	60	7.6×10^{-2}	5.4×10^{-5}
	100	3.2×10^{-1}	6.3×10^{-5}
	160	1.3×10^{-1}	6.1×10^{-4}
	245	8.4×10^{-2}	1.09×10^{-3}
	286	7.7×10^{-2}	1.53×10^{-3}
	390	6.2×10^{-2}	1.31×10^{-3}
	433	5.5×10^{-2}	1.18×10^{-3}
Shelfbreak	43	5.5×10^{-3}	8.7×10^{-5}
Shelfbreak	39	4.8×10^{-3}	8.9×10^{-5}

[a]Gulf Stream ratios corrected for Mn of crustal origin (crustal Mn:Al = 5.9×10^{-3} mol·mol^{-1}) (Taylor 1964).

3 pmol·L^{-1}, our current limit of detection. Regression of Cd (picomoles per litre) on phosphate (micromoles per litre) resulted in the expression $[Cd] = (212 \pm 21)[PO_4] - (49 \pm 21)$, $r^2 = 0.96$, for phosphate concentrations >0.3 μmol·L^{-1}. The Cd:phosphate ratio derived from this profile is lower than that derived from the Pacific data of Bruland (1980). Atlantic deep water Cd concentrations reported by Bruland and Franks (1983) were ~15% lower than predicted by Bruland's (1980) Pacific Cd:phosphate relationship. The Cd:phosphate relationship obtained in this work, if applied to Sargasso Sea deep water, would predict a Cd concentration about 25% lower than that observed by Bruland and Franks (1983). We tentatively attribute this difference to the shallower depth of the nutrient-depleted layer and hence deeper (relative to the nutrient distribution) regeneration of Cd from settling particulate matter. As Boyle et al. (1981) note, nutrient metal relationships can be expected to display regional variations which reflect differences in the physical, chemical, and biological parameters which control their relative distributions.

The high particulate Cd concentration at depths ≤100 m are suspect because of large analytical uncertainties associated with them. However, the vertical distribution of particulate Cd concentration roughly parallels that of particulate organic C (Table 3; Fig. 2). Particulate Cd concentrations in the Gulf Stream were similar to those observed by Wallace et al. (1977b) in Sargasso Sea surface waters (0.07–0.69 pmol·L^{-1}). Concentrations of particulate Cd below 100 m remained relatively constant despite a 35-fold increase in total dissolvable Cd and suggests little control of deepwater particulate Cd concentrations by ambient levels of dissolved Cd.

Total dissolvable Fe concentrations (Table 5), when corrected for particulate Fe concentrations, were relatively constant (~2 nmol·L^{-1}) with depth. Subtraction of particulate from total dissolvable Fe was justified because complete dissolution of particulate Fe is observed in shelf samples after storage for ~1 yr at pH 2 (G. T. Wallace, unpublished data). Greater than 90% of the total Fe in the shelf samples was in a particulate form. The operationally defined "soluble" Fe concentration of ~2 nmol·L^{-1} is more than an order of magnitude lower than the average oceanic value given in Brewer (1975). However, W. Landing and K. Bruland (University of

TABLE 5. Total dissolvable trace metal concentrations in the Gulf Stream.

Depth (m)	Cu (nmol·L^{-1})	Zn (nmol·L^{-1})	Ni (nmol·L^{-1})	Cd (pmol·L^{-1})	Fe (nmol·L^{-1})	Fe[b] (nmol·L^{-1})
30	0.98±0.07	0.30±0.08	2.5±0.4	<2.8	3.2±1.2	2.0±1.2
60	1.08±0.07	0.29±0.02	2.1±0.2	2.8±1.5	3.9±0.4	3.3±0.4
100	1.04±0.04	0.8±0.2[a]	2.4±0.1	8±2	2.4±0.4	1.9±0.4
160	0.83±0.03	0.30±0.02	3.0±0.4[a]	31±5	5.6±1.5	4.0±1.5[a]
245	0.96±0.15	1.20±0.17	2.7±0.1	68±9	4.0±1.2	2.4±1.2
286	1.02±0.05	2.5±1.2[a]	4.1±0.3[a]	93±9	6.9±3.2[a]	—
390	1.03±0.05	3.1±0.2[a]	4.4±0.4	230±30	5.4±0.5	1.6±0.6
433	0.92±0.10	1.29±0.14	5.3±0.4	282±28	4.5±0.9	—

[a]Contamination suspected or evident.
[b]Corrected for particulate trace metal concentration.

TABLE 6. Comparison of estimated atmospheric fluxes to the Gulf Stream with estimated first-order removal fluxes and corresponding residence times (τ) for the upper 100 m of the Gulf Stream (fluxes in nanomoles per square metres per day).

Element	From atmosphere	First-order removal	τ (yr)
Al	5000±1.8[a]	5000	0.15[b]
Fe	2100±1.7	2000	0.43
Mn	46±2.1	190	—
Cu	16±2.8	56	5.0
Ni	32±2.4	32	20
Cd	0.73±1.8	1.7	<0.6
Pb	29±1.5	26	—

[a]Geometric mean standard deviation reflecting variation in atmospheric concentrations observed by Mullins (1978).
[b]Particulate only.

California, Santa Cruz, CA, personal communication) found even lower soluble Fe concentrations in surface waters of the Pacific. This low concentration of soluble Fe is also consistent with the particle-reactive nature of Fe observed in MERL microcosms (Santschi et al. 1980).

Total dissolvable Zn concentration between 30 and 160 m was a uniform 0.3 nmol·L^{-1}. The surface concentration of Zn in the Sargasso Sea profile of Bruland and Frank (1983) was 0.04 nmol·L^{-1}, while concentrations at 100 and 375 m were 0.26 and 0.30 nmol·L^{-1}, respectively. Three of the eight samples collected suffered from obvious Zn contamination. Uncertainties in particulate Zn concentrations (Table 3) were uncomfortably high although the concentrations were similar to those reported by Wallace et al. (1977b) for Sargasso Sea surface waters.

Most of the samples were apparently contaminated with Pb during transfer and processing of the total dissolvable metal samples. Contamination was most likely to have occurred during handling and transfer on deck outside the confines of a controlled environment laboratory. However, particulate Pb values determined in separate subsamples of the original sample were thought to be reliable because (1) there was no correlation between total dissolvable Pb concentrations and particulate concentrations, (2) precision between replicates was good, (3) particulate Pb concentrations were comparable with those obtained in Sargasso Sea surface waters (Wallace et al. 1977b), and (4) particulate Pb concentrations in the upper 100 m were consistent with atmospheric and first-order removal fluxes estimated below. The somewhat higher Pb concentrations in the deeper samples may reflect scavenging by the Mn-rich particles present (Hem 1978; Bacon et al. 1980).

VERTICAL FLUX OF TRACE ELEMENTS IN THE GULF STREAM

Suspended element concentrations and the first-order removal rate constant determined from the vertical profile of Al (Wallace et al. 1981) were used to estimate the vertical downward flux of Fe, Mn, Ni, Cu, Cd, and organic C from the upper 100 m of the water column. Estimates of atmospheric inputs were calculated from the atmospheric concentration data of Mullins (1978) and respective elemental deposition velocities used by Wallace et al. (1977b).

Comparison of atmospheric and vertical fluxes in the water column (Table 6) indicate good agreement with the exception of Mn and possibly Cu. The removal of Mn exceeded atmospheric supply by a factor of four. Input of Mn from shelf waters (Landing and Bruland 1980; Martin and Knauer 1980) or the association of Mn with particles too small to be effectively removed by the biological mechanism proposed by Wallace et al. (1981) may explain the discrepancy. In view of the station's proximity to the shelf, the former possibility may be more probable.

Similarly, the discrepancies between the two fluxes for Cu (although not as dramatic due to the larger geometric standard deviation of the atmospheric Cu flux) may reflect a shelf source of Cu, as suggested by Boyle et al. (1981).

We have also estimated the first-order removal of particulate organic C for the upper 100 m by assuming C assimilation of the organisms responsible for the first-order removal to be between 30 and 70% of the C ingested. The calculated flux downward (in the form of rapidly settling feces) ranged between 1.08 and 2.5 mmol C·m^{-2}·d^{-1}. Assuming steady-state conditions, this loss in C must reflect the amount of "new" production and hence "new" N reaching the upper 100 m of the Gulf Stream (Eppley and Peterson 1979). From Eppley and Peterson's equation relating total production to new production, total production in the Gulf Stream is estimated to be on the order of 9.8−15 mmol C·m^{-2}·d^{-1}.

The "new" N required to offset this loss in C can be calculated assuming newly produced organic matter has a C:N molar ratio of 6.6 (Redfield 1934). A N flux between 160 and 380 μmol N·m^{-2}·d^{-1} is required. If this N is principally supplied in the form of nitrate diffusing upward, the gradient in nitrate concentration with depth (from Table 2) can be used to estimate the vertical eddy diffusion coefficient required to supply the nitrate flux. The range of required vertical eddy diffusion coefficients is 0.2−0.6 cm^2·s^{-1}. This range is consistent with recent estimates of vertical eddy diffusion coefficients in highly stratified regions of the water column (Jenkins 1980; White and Bernstein 1981) and provides further corroboration of the validity of the flux estimates made here.

Having estimated the vertical eddy diffusive coefficient, it is possible to reexamine the distribution of particulate Al below 100 m with the object of determining whether resuspension was the source of the observed profile. We approach this problem by estimating the resuspension flux from the vertical eddy diffusion coefficient given above and the observed concentration gradient of Al obtained by regression of particulate Al against depth between 100 and 433 m ($[Al]_p$ = 26 nmol·m^{-4} [Z] − 39 nmol·m^{-3}; r^2 = 0.93). We assume initially that the Al-bearing particles are neutrally buoyant and hence their upward transport by vertical eddy diffusion at a maximum. The maximum flux, using k_z = 0.4 cm^2·s^{-1} and the particulate Al concentration gradient, was 88 nmol Al·m^{-2}·d^{-1} or about 2% of the downward flux due to first-order removal from the upper 100 m. Furthermore, if we assign a realistic settling velocity of ~0.5 m·d^{-1} (Wallace et al. 1981) to Al-bearing particles at the top of the particulate Al concentration gradient (100 m), we see that the resulting downward flux of 165 nmol Al m^{-2}·d^{-1} (330 nmol·m^{-3} × 0.5 m·d^{-1}) exceeds that of the maximum upward vertical eddy diffusive flux by about a factor of two. It is therefore

unlikely that the vertical profile of particulate Al below 100 m reflects resuspension of particulate Al.

A second possibility considered was that the Al profile reflects disintegration of the large, rapidly settling particles falling from the upper 100 m of the water column. In this scenario the aggregated particulate Al is released as particles with their original diameters and a settling rate of ~0.5 $m \cdot d^{-1}$ (Wallace et al. 1981). If disintegration of the large particles leaving depths <100 m is complete by the time they reach 433 m and steady-state conditions are to be maintained, the vertical flux of small particulate aluminum at 433 m must equal atmospheric input. The product of the mass and mean settling velocity (0.5 $m \cdot d^{-1}$) of small particle Al at 433 m was 4.8 $\mu mol\ Al \cdot m^{-2} \cdot d^{-1}$, in excellent agreement with the 5.0 $\mu mol\ Al \cdot m^{-2} \cdot d^{-1}$ input from the atmosphere. Thus, the second scenario cannot necessarily be discounted although the apparent linearity of the increase in particulate Al with depth would be difficult to explain.

A third explanation invokes horizontal diffusion along isopycnals from their point of intersection with the bottom in the vicinity of the shelf break. Elevated concentrations of particulate Al at the shelf break have been observed (G. T. Wallace, unpublished data) and may well serve as a source of the particulate Al at depths >100 m in the Gulf Stream. The increase in concentration with depth may therefore reflect the shorter isopycnal distance to the sediment–water interface of successively deeper isopycnals in the Gulf Stream. Of the three scenarios, this latter one seems most acceptable to us but cannot be verified until the existence of isopycnal gradients of particulate Al can be demonstrated. Evidence supporting input of suspended matter from oceanic boundaries has been discussed by Armi (1978) and Brewer et al. (1980).

Residence Times

Where available data permit, residence times of metals in the upper 100 m of the Gulf Stream (Table 6) were calculated using first-order removal rates, also given in Table 6. Estimated residence times of Ni and Cu in the upper 100 m of the Gulf Stream are similar to those reported by Bruland (1980) for these elements (20 and 10 yr, respectively) in the upper 80 m of the eastern North Pacific. However, parameters controlling their residence times in the two oceans were different. Atmospheric and perhaps shelf inputs control Cu residence time in the Gulf Stream, while in the eastern North Pacific, atmospheric and eddy diffusive fluxes were more important. Nickel residence time in the eastern North Pacific was largely a function of eddy diffusive flux into the mixed layer, while both atmospheric and eddy diffusive flux (see below) were important in the Gulf Stream. Atmospheric input apparently controls the residence time of Fe in the upper 100 m of the Gulf Stream, as vertical gradients necessary to support an eddy diffusion flux of Fe to the upper 100 m were not detectable.

A significant eddy diffusive flux of Cd into the upper 100 m was calculated from the observed Cd:phosphate ratio and phosphate flux required to support new production in the upper 100 m of the Gulf Stream (Bruland 1980). When added to the atmospheric input, total input into the upper 100 m equaled 2.9 $nmol \cdot m^{-2} \cdot d^{-1}$, which was still within a factor of two of the first-order removal flux estimate. The residence time of Cd in the 80-m mixed layer of the Pacific, estimated by Bruland (1980), was 0.1 yr or about 6 times shorter than that estimated here.

An eddy diffusive flux of ~10 $nmol\ Ni \cdot m^{-2} \cdot d^{-1}$ into the upper 100 m was estimated in an analogous manner using the Ni:phosphate relationship given by Bruland (1980). Because atmospheric deposition (32 $nmol \cdot m^{-2} \cdot d^{-1}$) still remained the dominant source of Ni in the upper 100 m, agreement between total input and first-order removal of Ni was not seriously altered.

Discussion

Removal of Fe, Ni, Cd, and Pb in association with rapidly settling particulate matter appears to balance atmospheric and vertical eddy diffusive fluxes of these elements into the upper 100 m of the Gulf Stream. Particulate fluxes of Mn and perhaps Cu exceed atmospheric input and suggest an additional source of these metals. We wish to emphasize the tentative nature of the flux estimates presented here, as they involve making a number of as yet untested assumptions and use of a rather limited data set.

Wallace et al. (1977b) estimated that atmospheric input of a number of metals into Sargasso Sea surface waters was roughly balanced by downward metal fluxes in association with settling particulate organic matter. Buat-Menard and Chesselet (1979) compared atmospheric inputs to the tropical North Atlantic with downward fluxes of metals in association with both large and small particles. The major components of Buat-Menard and Chesselet's downward flux was associated with the flux of large particles. Their large-particle fluxes were estimated using the particulate organic C flux of Wallace et al. (1977b) and calculated metal to C ratios for the large particles. In contrast with the results of Wallace et al. (1977b), the model of Buat-Menard and Chesselet (1979) revealed considerable differences between atmospheric input and the downward particle flux, the latter exceeding the former by an order of magnitude for some elements.

The source of the differences between the two models lies in the choice of metal:carbon ratios used in estimating the downward large particle flux. Wallace et al. (1977b) used metal:carbon ratios calculated from particulate matter collected on 0.4-μm Nuclepore filters (metals) and Reeve Angel 984H glass fiber filters (carbon). Both types of filters have been shown to have similar retention efficiencies (Sheldon 1972). Metal:carbon ratios used by Buat-Menard and Chesselet (1979) were calculated from the concentration of metals also collected on 0.4-μm Nuclepore filters. Particulate organic C concentration data were estimated from the data of Krishnaswami and Lal (1977), which were obtained using cotton fiber filters, which gave almost quantitative recovery for particles >5 μm in diameter and ~60% recovery for particles between 0.5 and 1.2 μm in diameter. From the data of Buat-Menard and Chesselet (1979) it can be calculated that the particulate organic C concentration, used in their calculation of the metal:carbon ratios to estimate their large-particle flux, was ~6 $\mu g \cdot L^{-1}$. In contrast, the average measured particulate organic C concentration used by Wallace et al. (1977b) was 26 $\mu g \cdot L^{-1}$. Consequently, all other parameters

TABLE 7. Comparison of "primary" sediment trap flux of Spencer et al. (1978) in the Sargasso Sea with estimated first-order removal flux derived from Gulf Stream data (fluxes in nanomoles per square metre per day).

Element	Primary flux	First-order removal flux
Al	5100	5000
Fe	2600	2000
Mn	249	190
Cu	69	56

being equal, Buat-Menard and Chesselet's (1979) choice of particulate organic C concentration resulted in about a four-fold increase in downward particle-associated metal flux and largely accounts for the differences between their atmospheric and particle-associated metal flux estimates.

The validity of the vertical flux model developed here for the Gulf Stream is strengthened by its ability to predict both a C flux consistent with independent estimates of "new" production in transitional waters (Eppley and Peterson 1979) and a vertical eddy diffusion coefficient of the same magnitude as other independent estimates of this parameter for well-stratified water columns. Thus, the chemical fluxes predicted are consistent with both the biological and physical characteristics of the water column.

There is remarkable similarity between the vertical first-order removal fluxes of Al, Fe, Mn, and Cu estimated here and the "primary" green fecal pellet sediment trap fluxes of these same elements observed by Spencer et al. (1978) (Table 7). The agreement suggests that the processes producing the large particle fluxes may be relatively uniform over large areas of the tropical North Atlantic and lends support to the large-particle model of Spencer et al. (1978).

Several observations can be made concerning the vertical distribution of particulate matter and potential carrier phases. With the exception of Fe there was little similarity between the vertical distribution of particulate Al and the other elements measured. Ratios of Fe:Al were close to crustal and, with the possible exception of the sample at 100 m, there was little evidence for the presence of a hydrous iron oxide phase.

The distinctly different trends in particulate Mn and Al concentrations, especially in the upper part of the water column, suggest little association between aluminosilicate and Mn solid phases. Consequently, we believe the high Mn:Al ratios observed primarily reflect association of Mn with particulate organic matter, concurrent oxidation of both manganese and organic matter below the DCM, and association of oxidized manganese with refractory particulate matter. This hypothesis is supported by the systematic increase in particulate Mn with decrease in particulate C (-0.26 nmol $Mn \cdot \mu mol\ C^{-1}$) between 100 and 245 m.

The uniformity in the vertical concentration of particulate Ni, Cu, and Cd suggests little association with either aluminosilicate or Mn solid phases. Furthermore, the increases in Ni and Cd concentration with depth in the water column are not reflected in their particulate counterparts and suggests that the adsorptive affinity of the particles for these metals is quite small.

In conclusion, the concentrations of a number of trace elements in the surface layer of the Gulf Stream are particularly sensitive to atmospheric inputs. Total dissolvable and particulate metal concentrations are comparable with concentrations of these metals recently measured in open-ocean Atlantic and Pacific vertical profiles, suggesting little influence by exchange with adjacent shelf waters. However, vertical flux estimates suggest that significant inputs of total dissolvable Cu and Mn and particulate Fe and Al to the Gulf Stream may be occurring.

Prediction of the effects of enhanced atmospheric or shelf inputs of metals into the biologically important surface layer of the Gulf Stream will require further information on the adsorptive characteristics of the particles present and assessment of the sensitivity of the biological processes believed to be responsible for the generation of the large-particle flux.

Acknowledgments

Discussions with Ken Bruland, Ed Boyle, Jim Yoder, and Bob Duce were most useful in development of this manuscript. We also thank Linda Land, Beth Christiansen, and Kim Navia for typing the manuscript and Suzanne McIntosh for drafting the figures. This research was sponsored by U.S. Department of Energy contract DE-AS09-76EV00890.

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Role of Marine Phytoplankton in Determining the Chemical Speciation and Biogeochemical Cycling of Arsenic[1]

JAMES G. SANDERS

Academy of Natural Sciences, Benedict Estuarine Research Laboratory, Benedict, MD 20612, USA

SANDERS, J. G. 1983. Role of marine phytoplankton in determining the chemical speciation and biogeochemical cycling of arsenic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 192–196.

Biological mediation of arsenic speciation in marine systems is substantial and significant. Phytoplankton reduce and methylate arsenic, thus altering its geochemical cycle. Rates of arsenic reduction and methylation are proportional to the primary productivity of the ecosystem. In highly productive ecosystems, up to 80% of the total arsenic pool may undergo reduction and methylation. Experiments detailing rates of reduction have been performed in controlled marine ecosystems. Predictions of arsenic speciation based on these results agree well with actual samples taken from coastal areas. The form of reduced arsenic present varies between regions and temporally within regions, probably because of differences in phytoplankton community structure.

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Il se produit, dans les systèmes marins, une importante spéciation arsenicale par action biologique. Le phytoplancton réduit et méthyle l'arsenic, altérant ainsi son cycle géochimique. Les taux de réduction et de méthylation de cet élément sont proportionnels à la productivité primaire de l'écosystème. Dans des écosystèmes fortement productifs, jusqu'à 80 % de la quantité totale d'arsenic peuvent être réduits et méthylés. On a mené dans des écosystèmes marins standardisés des expériences permettant de préciser les taux de réduction. Les prédictions touchant la spéciation de l'arsenic, fondées sur ces résultats, s'accordent bien avec les échantillons prélevés dans les régions côtières. La forme de l'arsenic réduit présent varie d'une région à l'autre et, dans le temps, au sein des régions, probablement par suite de différences de structure des communautés planctoniques.

Received March 18, 1982
Accepted October 7, 1982

Reçu le 18 mars 1982
Accepté le 7 octobre 1982

THE world's oceans have a capacity for transformation and assimilation of toxic substances and have served as a "mixing pot" for billions of years. This capacity is not limitless, but, unfortunately, we do not know how large it is for most compounds. One such compound, arsenic, is ubiquitous in nature, present in water and soils and concentrated in a variety of ores. It is quite toxic to organisms; indeed, its primary commercial use is as a pesticide (Mackenzie et al. 1979). Because of industrial use, and also due to loss during mining of metal ores, anthropogenic input of arsenic to the world's oceans has increased greatly during the past 100 yr (Mackenzie et al. 1979). Arsenic is also emitted during coal and oil combustion (Gordon and Zoller 1974). In addition, stream loads of arsenic have increased in modern times because of agricultural and deforestation activities (Judson 1968; Garrels and Mackenzie 1971). If present activities continue, emissions of arsenic will have doubled in the period 1970–83 (Lee and Duffield 1979) and arsenic concentrations in surface waters of the oceans will increase approximately 2% by the year 2000 (Mackenzie et al. 1979). Although an overall increase of 2% in 20 yr is not overwhelming, this burden will not be spread evenly and will be much greater in estuaries and coastal oceans. Because of this impact, an understanding of arsenic geochemistry in coastal systems is extremely important.

Arsenic in oxidized, aquatic systems is present primarily as an inorganic ion, arsenate (Waslenchuk 1978; Sanders 1980). Although reduced arsenic (arsenite) is more toxic and is the form used in pesticides (Peoples 1975), arsenate is likely to have the greatest impact at low concentrations. It is chemically similar to phosphate and is readily taken up by phytoplankton (Sanders and Windom 1980). Once arsenate is inside the cell, oxidative phosphorylation and growth are inhibited, causing a decrease in overall primary productivity (Sanders 1979; Planas and Healey 1978). However, work in my laboratory has indicated that all species of phytoplankton are not equally sensitive to arsenate; some are inhibited at levels just

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6862)
Imprimé au Canada (J6862)

TABLE 1. Rates and magnitude of arsenic reduction in phytoplankton cultures grown under ambient and elevated (6 $\mu g \cdot L^{-1}$) concentrations of arsenic.

Culture type, location	Ambient As		Elevated As	
	Arsenate reduction ($ng \cdot L^{-1} \cdot d^{-1}$)	Maximum % arsenic reduced	Arsenate reduction ($ng \cdot L^{-1} \cdot d^{-1}$)	Maximum % arsenic reduced
Batch	85	85	575	85
CEE[a] (CEPEX)[b]	—	—	100	28
CFM[c] (MERL)[d]	1	9	—	—
CFM (WHOI)[e]	—	—	101	11
SCC[f] (Chesapeake Bay)	45	84	67	8

[a]Controlled Ecosystem Enclosure.
[b]From Sanders and Windom (1980) and Windom and Sanders (1981).
[c]Continuous-flow microcosm.
[d]Extracted from Johnson and Burke (1978).
[e]From Sanders and Vermersch (1982).
[f]Semicontinuous culture.

exceeding ambient concentrations of arsenate in the oceans, while others are resistant to arsenate concentrations two orders of magnitude higher (Sanders and Vermersch 1982). Within the phytoplankton community, where rapid growth and species succession are normal occurrences, low levels of arsenate can shift dominance toward resistant forms instead of causing an overall decrease in productivity, as has been measured in laboratory cultures (Sanders 1979; Planas and Healey 1978). These postulated shifts in phytoplankton community structure have profound impacts upon the biota of the entire ecosystem. Of even greater interest, these shifts may also affect the chemical speciation of a bioactive element such as arsenic. Even though the biota contain only minor amounts (<0.1%) (Sanders 1980) of the total arsenic in marine systems, the impact of these organisms upon the chemical structure of arsenic can be quite substantial. Phytoplankton take up arsenate indiscriminately but do not retain large quantities within tissues. Most of the arsenic is released to the surrounding water in chemically altered form. The rate of uptake and release, the chemical alteration that takes place, and the relative importance of this biological intervention in arsenic geochemistry throughout the coastal North Atlantic Ocean are the subjects of this article.

Materials and Methods

Estuarine and coastal phytoplankton were maintained under a variety of culture conditions in various locations in the United States and Canada. These include studies that utilized batch cultures of algal clones under constant environmental conditions and varying concentrations of arsenic (Sanders and Windom 1980), semicontinuous cultures under similar conditions (Chesapeake Bay, this study), static cultures in large bags or "controlled ecosystem enclosures" (CEPEX) (Sanders and Windom 1980; Windom and Sanders 1981), and continuous-flow microcosms (MERL, Burke 1978; Johnson and Burke 1978; Vineyard Sound, MA, Sanders and Vermersch 1982). I have included studies from the CEPEX site because environmental conditions and phytoplankton community structure are similar to coastal North Atlantic regions. Experimental scope and design varied in each of the above, but in each study, changes in the chemical speciation of arsenic within the systems with respect to phytoplankton growth were monitored through time. Phytoplankton growth was determined in all studies by calculating specific growth rates from frequent cell counts. In addition, rates of carbon incorporation by phytoplankton were determined in several studies (batch cultures, CEPEX, Vineyard Sound). Further details concerning experimental design can be obtained from the references cited above.

In all studies, measurement of the separate arsenic species was performed on aqueous samples using the DC arc-induced plasma emission technique after hydride formation (Braman et al. 1977). The detection limit is approximately 0.5 ng for arsenite and arsenate and 1 ng for methyl arsenicals. The maximum sample size used was 40 mL, giving minimum detectable concentrations of 0.01 and 0.03 $\mu g\ As \cdot L^{-1}$, respectively. The precision for aqueous samples based on replicate analyses is approximately 10%.

In addition to experimental manipulations, data bases containing information on arsenic concentration and speciation are available from these locations over time. Therefore, temporal and spatial variability in arsenic speciation can be examined and correlated with phytoplankton productivity and/or species composition.

Results and Discussion

Arsenic Uptake and Reduction

In all cases, algal growth was accompanied by an increase in the proportion of reduced arsenic within the surrounding medium; however, the rate and magnitude of reduction varied widely (Table 1). The arsenic reduction rate discussed here is an "apparent" one. Arsenite produced during reduction is continuously reoxidized; therefore, actual reduction rates are somewhat higher than measured here.

Arsenic reduction within MERL (Marine Ecosystems Research Laboratory) microcosms was erratic and slow: up to 1 $ng \cdot L^{-1}$ of arsenic was reduced per day, with an apparent average reduction rate of 0.25 $ng \cdot L^{-1} \cdot d^{-1}$ (calculated from Johnson and Burke 1978). Less than 9% of the arsenic was

TABLE 2. Arsenate reduction by phytoplankton (ng As(V) reduced·10^6 cells^{-1}·d^{-1} or ng As(V) reduced·mg C^{-1}·d^{-1}) in experimental cultures under ambient and elevated (6 μg·L^{-1}) levels of arsenate.

Culture type, location	Dominant algae	ng·10^6 cells^{-1}·d^{-1}		ng·mg C^{-1}·d^{-1}	
		Ambient	Elevated	Ambient	Elevated
Batch	*S. costatum*, centric diatoms	2	17	—	190
CEE (CEPEX)	Flagellates, dinoflagellates	—	—	—	220
CFM (MERL)	—	1.7	—	—	—
CFM (WHOI)	*S. costatum*, *Nitzschia seriata*	—	30	—	290
SCC (Chesapeake Bay)	*S. costatum*, *Chromulina* sp.	3.7	14	—	—

TABLE 3. Concentration and chemical speciation of arsenic (μg·L^{-1}), including % reduced, in Chesapeake Bay samples relative to cell density (×10^6 cells·L^{-1}).

Date	Cell density	As(V)[a]	As(III)[b]	MMA[c]	DMA[d]	Total	% reduced
Feb. 20	6.4	0.11	0.02	0.02	0.49	0.64	83
Apr. 13	10.8	0.19	0.03	0.05	0.54	0.81	77
May 28	12.0	0.18	0.02	0.04	0.65	0.89	80
June 29	3.2	0.45	0.06	0.07	0.41	0.99	55
Aug. 7	6.7	0.66	0.03	0.27	0.23	1.19	45
—	7.4	1.20	0.08	0.16	0.16	1.60	25
—	6.6	1.26	0.06	0.27	0.02	1.61	22
Sept. 9	2.4	1.30	0.03	0.02	0.05	1.40	7
Sept. 17	1.6	1.22	0.06	0.02	0.03	1.33	8
—	1.0	0.92	0.03	0.01	—	0.96	4
—	4.6	0.50	—	0.05	0.06	0.61	18

[a]Arsenate.
[b]Arsenite.
[c]Methylarsonic acid.
[d]Dimethylarsinic acid.

present in a reduced form at any time (Johnson and Burke 1978). In contrast, batch cultures of *Skeletonema costatum* grown under conditions of phosphorus limitation exhibited arsenic reduction rates of 85 ng·L^{-1}·d^{-1} at ambient concentrations of arsenic and rates in excess of 500 ng·L^{-1}·d^{-1} at an elevated arsenic concentration of 6 μg·L^{-1} (Sanders and Windom 1980). Up to 80% of the arsenic was present in reduced form after 7 d of growth (Sanders and Windom 1980). The rates of reduction in the various experiments are not comparable; however, when viewed in relation to relative quantities of phytoplankton biomass present instead of in volumetric terms (Table 2), the rates become quite similar. Arsenate reduction by phytoplankton cultured under differing environmental conditions but at ambient concentrations of arsenic varied between 2 and 4 ng·10^6 cells^{-1}·d^{-1}. Algal clones and natural phytoplankton assemblages grown at elevated concentrations of arsenic also exhibited similar reduction rates, 14–30 ng·10^6 cells^{-1}·d^{-1}, or 200–300 ng·mg C^{-1}·d^{-1}. The close agreement of these rates may well be fortuitous but still illustrates the striking similarities between algae growing at widely separated locales.

CHEMICAL FORM OF REDUCED ARSENIC

The simplest form of reduced arsenic in natural waters is arsenite; however, significant quantities of other compounds, particularly methylarsonic (MMA) and dimethylarsinic (DMA) acids, are often present (Andreae 1978; Waslenchuk 1978; Sanders 1980). All of these compounds can originate from biological activity. Interestingly, not all algae produce and release the same compounds. *Skeletonema costatum*, a centric diatom commonly important in coastal phytoplankton communities, produced only arsenite and DMA in culture (Sanders and Windom 1980). Other diatoms produced the same compounds, with two also producing small amounts of MMA (Andreae 1978; Andreae and Klumpp 1979). Coccoliths grown under similar conditions produced MMA in larger quantities (Andreae and Klumpp 1979). The natural phytoplankton assemblages discussed here produced similar compounds, primarily DMA, with some arsenite and traces of MMA. Arsenite was the only measurable reduced compound in the MERL microcosms (D. L. Johnson, State University of New York, Syracuse, NY, personal communication). Chesapeake Bay cultures grown at elevated levels of arsenate produced significant amounts of MMA, up to 270 ng·L^{-1}. For the most part, the assemblages were composed of *S. costatum* and other diatoms (Table 2); occasional flagellate blooms (especially in the Chesapeake Bay and CEPEX experiments) occurred.

In addition to the experimental cultures, a number of sam-

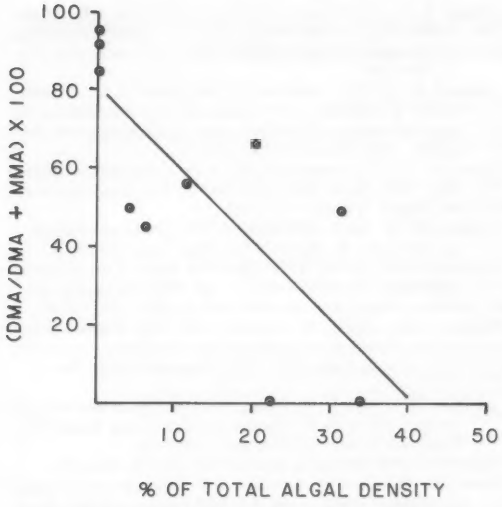

FIG. 1. The ratio of DMA to MMA (ratio = (DMA/DMA + MMA) × 100) in relation to the abundance of *Thalassiosira* sp. ("*T. pseudonana*" type, as percentage of total algal assemblage). The equation for the regression is $Y = -1.99X + 81.2$ ($r = 0.76$, $P < 0.01$).

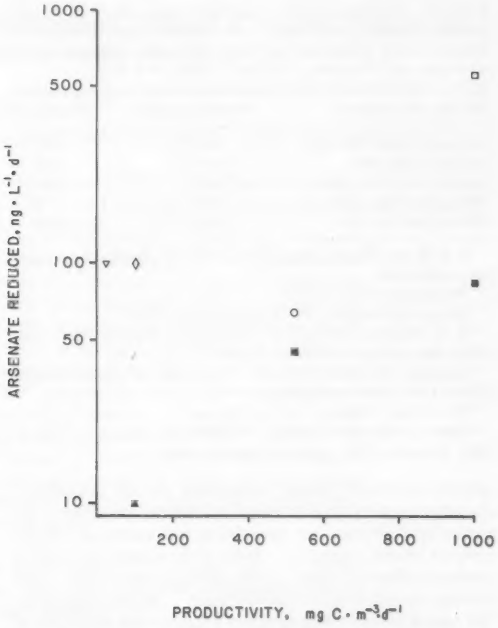

FIG. 2. The rate of arsenate reduction (nanograms per litre per day) in experimental algal cultures maintained at ambient (solid symbols) and elevated (open symbols) concentrations of arsenic. ■,□, *S. costatum* batch cultures; ●,○, Chesapeake Bay phytoplankton assemblages; ▲, MERL microcosms; ◇, CEPEX enclosures; ▽, WHOI microcosms.

ples were taken from the mesohaline region of the Chesapeake Bay throughout the winter, spring, and summer to see if the chemical speciation of arsenic within the samples correlated with the dominant phytoplankton groups and genera present (Table 3). The percentage of reduced arsenic in these samples was very high, 70–80%, during late winter and spring, when algal densities are generally at their peak (Mulford 1972; R. A. Mulford, Academy of Natural Sciences of Philadelphia, Philadelphia, PA, personal communication). Summer values were much lower: 7–42% of the arsenic was reduced, with an average value of 29%. The correlation between cell densities and the percentage of arsenic present in reduced form (Table 3) is quite high ($r = 0.75$, $P < 0.01$).

The chemical composition of this reduced arsenic varied in an irregular fashion. Arsenite was rarely present in significant quantities and never comprised more than 5% of the total arsenic. DMA, on average, was the predominant reduced form present, varying from 2 to 74% of total arsenic. MMA was present in all samples and varied between 1 and 23%. The ratio of DMA to MMA (ratio = (DMA/DMA + MMA) × 100) did not remain constant but varied between 0 and 96. Changes in this ratio should correspond to discernible changes in either dominant algal groups (pennate diatoms, centric diatoms, dinoflagellates, etc.) or perhaps to changes in dominant species of phytoplankton. No relationship between algal groups and the form of methylated arsenic was evident; however, large quantities of MMA were present when one species of centric diatom was present in appreciable numbers. This relationship is shown in Fig. 1; the correlation between the two is significant ($r = 0.76$, $P < 0.01$). The diatom is a species of *Thalassiosira*, similar in form to *T. pseudonana*, and is a common and sometimes dominant member of the phytoplankton community in Chesapeake Bay (Mulford 1972). It is not one of the most important species, however, and its correlation with the ratio of methylated arsenicals may be circumstantial.

The relatively large quantity of arsenic present as MMA is unusual. Other regions sampled for arsenic generally contain only traces of MMA; only rarely does it comprise more than 1% of the total. Chesapeake Bay, therefore, is unusual both in the large amount of reduced arsenic present and in its form. The reasons for these anomalies are not fully understood but are likely caused by the very high rates of primary production that occur within the Bay, up to 800 g $C \cdot m^{-2} \cdot yr^{-1}$ (W. R. Boynton, University of Maryland, Solomons, MD, personal communication). The shallow nature of the Bay may also be a factor; this still needs to be investigated.

IMPORTANCE OF BIOTIC INTERVENTION IN THE ARSENIC CYCLE

It is apparent that the intervention of phytoplankton in the cycling and chemical composition of arsenic in marine systems is significant and can in some instances become quite important. It is obvious that phytoplankton can control the

TABLE 4. Average quantity of reduced arsenic (% ± SD of total arsenic) in surface water samples from coastal regions in relation to annual primary production (g $C \cdot m^{-2} \cdot yr^{-1}$). The equation for the regression is $Y = 0.085X - 6.61$ ($r = 0.83$, $P < 0.05$).

Site (No. of samples)	% reduced arsenic	Production
Vineyard Sound, MA (4)	4±3	150[a]
Georgia Bight (16)	12±7[b]	200[c]
Saanich Inlet, B.C. (4)	21±5	225[d]
Narragansett Bay (29)	7±3[e]	270[f]
Chesapeake Bay (12)	33±30	450[g]

[a]J. H. Ryther, Harbor Branch Foundation, Ft. Pierce, FL, personal communication.

[b]Waslenchuk (1977, 1978).

[c]Haines and Dunstan (1975); Bishop et al. (1980).

[d]G. T. Wallace, University of Massachusetts, Boston, MA, unpublished data and personal communication.

[e]Inorganic (As(III), As(V)) only. No organic compounds detected (Burke 1978; Johnson and Burke 1978).

[f]Oviatt et al. (1981).

[g]Kemp and Boynton (1980); J. A. Mihursky, University of Maryland, Solomons, MD, personal communication.

quantity of reduced arsenic compounds present; in addition, the structure of the phytoplankton community may control the presence or absence and the relative importance of various reduced arsenic compounds. Both of these processes have a profound effect on arsenic geochemistry, its rate of movement through aquatic systems, and its toxicity to aquatic organisms. We cannot yet state with authority which groups or species of algae are important in determining the reduced compounds present, although we are beginning to see patterns develop. We can, however, predict in a general sense the rates of arsenate reduction likely to occur in a given area. Figure 2 illustrates the significant correlation that occurs between the rate of arsenic reduction and the rate of primary production in experimental systems at ambient and elevated concentrations of arsenic. With these data (hopefully only as a starting point), we can calculate the likely reduction rate for an area subject to present or future arsenic inputs, giving us a first impression of the possible impact and toxicity of that arsenic to the biota.

We can also predict the quantity of arsenic that will be reduced, on average, relative to annual primary productivity. This information is available for a number of coastal areas of the North Atlantic (plus Saanich Inlet, B. C.) (Table 4). The relationship between the average quantity of arsenic that is present in reduced form and the annual productivity of the region is striking and hopefully will be of some value in future determinations of the possible fates and effects of arsenic inputs to the coastal ocean.

Acknowledgments

This research was supported by the National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment (grant No. NA81RAD00032), and by the Academy of Natural Sciences.

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Regulation of Zn^{2+} Uptake from the Gastrointestinal Tract of a Marine Teleost, the Winter Flounder (*Pseudopleuronectes americanus*)[1]

M. A. SHEARS AND G. L. FLETCHER

Marine Sciences Research Laboratory, Memorial University of Newfoundland, St. John's, Nfld. A1C 5S7

SHEARS, M. A., AND G. L. FLETCHER. 1983. Regulation of Zn^{2+} uptake from the gastrointestinal tract of a marine teleost, the winter flounder (*Pseudopleuronectes americanus*). Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 197–205.

The gastrointestinal uptake of Zn^{2+} was studied in winter flounder (*Pseudopleuronectes americanus*) using an *in situ* technique. The entire digestive tract was capable of absorbing Zn^{2+}, with the uppermost portion of the intestine having the highest and the stomach the lowest capacity. A seasonal study revealed that the capacity of the digestive tract to absorb Zn^{2+} was greatest during the summer months. At least two steps appeared to be involved in the absorption process, the first a rapid accumulation of Zn^{2+} by the tissue, and the second a slower transfer into the body. The amount of Zn^{2+} absorbed increased with increasing loads of Zn^{2+} in the lumen; the transfer mechanism(s) was not saturated at the highest Zn^{2+} loads tested. Zn^{2+} uptake was inhibited in the presence of Cu^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}, and Hg^{2+}. The capacity of the digestive tract to absorb Zn^{2+} was not affected by feeding the flounder a high-Zn^{2+} diet or by increasing body Zn^{2+} loads by intravenous injections. It is suggested that elimination mechanisms may play a greater role in maintaining Zn^{2+} homeostasis than controlling gastrointestinal uptake.

SHEARS, M. A., AND G. L. FLETCHER. 1983. Regulation of Zn^{2+} uptake from the gastrointestinal tract of a marine teleost, the winter flounder (*Pseudopleuronectes americanus*). Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 197–205.

L'absorption gastro-intestinale de Zn^{2+} chez la plie rouge (*Pseudopleuronectes americanus*) a été étudiée *in situ*. Le tractus digestif entier peut absorber cet élément, la portion supérieure de l'intestin au plus haut degré et l'estomac au plus bas. Les résultats d'une étude saisonnière indiquent que la capacité d'absorption de Zn^{2+} du tractus digestif est maximale durant les mois d'été. Il semble y avoir, dans le processus d'absorption, au moins deux étapes : dans un premier temps, une rapide accumulation de Zn^{2+} par le tissu, et dans un second, le transfert, plus lent, dans le corps. La quantité absorbée augmente en fonction des charges de Zn^{2+} dans la lumière; le ou les mécanismes de transfert ne sont pas saturés aux plus hautes charges de Zn^{2+} utilisées. La présence de Cu^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+} et Hg^{2+} entrave l'absorption de Zn^{2+}. La capacité du tractus digestif à absorber Zn^{2+} n'est pas influencée par un régime alimentaire riche en cet élément offert aux plies, ou en augmentant les charges par injection intraveineuse dans le corps. Nous croyons que les mécanismes d'élimination jouent un rôle plus important que l'absorption gastro-intestinale dans le maintien de l'homéostasie de Zn^{2+}.

Received March 19, 1982
Accepted October 13, 1982

Reçu le 19 mars, 1982
Accepté le 13 octobre 1982

ALTHOUGH zinc exerts sublethal and lethal effects on fish when it is present in excess amounts in freshwater and marine environments (Spear 1981), it is also essential in trace amounts for their normal growth and development (Ogino and Yang 1978, 1979; Ketola 1979). Fish accumulate zinc from both water and dietary sources. However, laboratory studies using ^{65}Zn indicate that diet is normally the main source of Zn^{2+} in marine fish (Renfro et al. 1975; Hoss 1964; Pentreath 1973a, 1973b).

Since Zn^{2+} is an essential element it is generally thought that homeostatic mechanisms must operate to control body levels in fish. However, evidence for this is largely circumstantial and there is little known about the extent of or the mechanisms involved in its regulation. The lack of significant differences in tissue concentrations of the same species of fish sampled in habitats containing a wide range of heavy metal contamination implies some form of regulation (Northcote et al. 1975; Uthe and Bligh 1971; Goodyear and Boyd 1972; Topping 1973; Eustace 1974; and Greig and Wenzolf 1977). Another indication of the ability of fish to regulate Zn^{2+}

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6863)
Imprimé au Canada (J6863)

comes from the observation that within the same species, differences in tissue concentrations occur due to the sex (Chernoff and Dooley 1979; Fletcher and King 1978), the size (Chernoff and Dooley 1979; Cross et al. 1973; Milner 1979), and the season when sampled (Fletcher and King 1978; Milner 1979).

In mammals and birds, Zn^{2+} homeostasis is thought to be maintained by mechanisms operating at the sites of absorption and secretion in the gastrointestinal tract (Becker and Hoekstra 1971). Since it appears that most Zn^{2+} enters marine fish via the digestive tract, it appears reasonable to postulate that similar mechanisms operate in fish. The primary aim of the present study was to assess the role of the gastrointestinal tract in Zn^{2+} regulation in fish. Towards this end, several factors known to influence Zn^{2+} absorption in mammals were examined in winter flounder (*Pseudopleuronectes americanus*).

Materials and Methods

Winter flounder (25–45 cm long, 250–1000 g) were collected by divers equipped with SCUBA (Fletcher 1977). In the laboratory, the fish were maintained in aquaria (250–40 000 L) supplied with flowing seawater under conditions of ambient temperature and photoperiod. They were fed chopped capelin throughout the feeding period of April–October (Fletcher and King 1978). Except where indicated, the experiments were conducted during this period. The fish were not fed for 5–7 d prior to surgery to allow the intestine to empty. An in situ technique used to study gastrointestinal uptake of Zn^{2+} in mammals (Hamilton et al. 1978; Van Campen 1969) was modified to study similar parameters in fish.

Fish were placed in anaesthetic (0.5 g of tricaine methanesulfonate (MS 222) in 4 L seawater) for approximately 10 min and a 1:2 dilution of the same solution or clean seawater was passed over the gills during surgery. An incision was made in the body wall to expose the gastrointestinal tract. A segment of the tract was then tied off, and a fixed volume (0.50–0.55 mL) of saline solution (1% NaCl) containing the radiotracer ^{65}Zn (New England Nuclear) and where indicated $ZnCl_2$ as well as other test substances were injected into the ligated region. The incision was sutured and the fish was returned to the aquarium. After a specified time the fish was killed by a blow on the head and bled from a caudal blood vessel, and the ligated segment was dissected out of the body. The contents in the lumen of the ligated segment were emptied into a counting vial. The tissue was placed in a separate vial and both samples were counted in a gamma scintillation counter (Packard model 578).

The results were expressed as the amount of Zn^{2+} accumulated in the intestinal tissue (based on the counts per minute (cpm) ^{65}Zn in the tissue) and the amount of Zn^{2+} transferred across the digestive tract into the body. The latter was computed by subtracting the sum of the cpm ^{65}Zn in the intestinal tissue and in the intestinal lumen contents from the total cpm ^{65}Zn injected into the tied-off segment. When a load of $ZnCl_2$ was injected with the isotope, the results were converted to micrograms of Zn^{2+} based on the specific activity of the ^{65}Zn injection.

The in situ technique was initially used to determine the site(s) of zinc uptake in the gastrointestinal tract. As described above, ^{65}Zn (plus $ZnCl_2$ where indicated) was injected into the stomach, the upper intestine (which included the pyloric appendages), the midportion of the intestine, and the lower intestine (excluding the rectum) and left for 7–8 h.

This method was also used to study several factors that might affect the extent of Zn^{2+} uptake. In examining these parameters only one segment of the intestine, the uppermost portion including the pyloric appendages, was tied off.

To describe the time course of Zn^{2+} uptake from the intestinal tract, ^{65}Zn and a 52-μg Zn^{2+} load were injected into the upper intestine and left for periods ranging from 1 to 48 h ($n = 5–7$ fish per time period).

The effect of the amount of Zn^{2+} in the intestinal lumen on both the accumulation of Zn^{2+} in the tissue, and the transfer into the body, was examined for a fixed time period (4–7 h) at various Zn^{2+} loads (minimum of five fish for each Zn^{2+} load).

The in situ technique was also used to test the effect of an excess of another metal (200 μg as its chloride, n = number of fish: Cu^{2+}, $n = 15$; Mg^{2+}, $n = 10$; Ca^{2+}, $n = 10$; Ni^{2+}, $n = 9$; Fe^{3+}, $n = 10$; Mn^{2+}, $n = 5$; Hg^{2+}, $n = 9$; Co^{2+}, $n = 6$; Cd^{2+}, $n = 10$; Cr^{2+}, $n = 10$) on Zn^{2+} (5 μg) uptake (exposure period = 4–5 h). The effect of Cu^{2+} on Zn^{2+} (5 μg) uptake was further examined using copper loads ranging from 10–200 μg ($n = 5$ fish per load). The statistical significance of the effects of these metal loads on Zn^{2+} accumulation in the intestinal tissue and on Zn^{2+} transfer into the body was determined by analysis of variance and the least significant difference (lsd) test (Steele and Torrie 1960).

The seasonal in situ uptake of Zn^{2+} (55-μg Zn^{2+} load, exposure period = 5–7 h) was examined at monthly intervals over a 2-yr period. Fish used in this study were collected from Conception Bay, Nfld., and were held in the laboratory for approximately 1 wk before being tested. They were not fed during this time.

To test the effect of diets with varying Zn^{2+} content on Zn^{2+} uptake, fish were fed food pellets (40% moisture) consisting of Silver Cup Fish Feed, manufactured by Murray Elevators, Murray, UT (guaranteed analysis: crude protein, 38%; crude fat, 5%; crude fibre, 7%; ash, 15%; with additions of cod liver oil, 2%; carboxymethylcellulose, 3%; distilled water) containing 60 μg Zn^{2+}/g wet wt (control) or pellets with $ZnCl_2$ added (600 μg Zn^{2+}/g wet wt). Both groups were fed the control diet for 2 wk, followed by the control or high-Zn^{2+} diet for 5 wk at a rate of approximately 2% of their body weight per day. After allowing 6 d for the gut to clear, the in situ technique was used to compare uptake of Zn^{2+} (52-μg Zn^{2+} load) in the two groups (exposure period = 7–9 h). The stable Zn^{2+} concentrations (micrograms of Zn^{2+} per gram dry weight) of nitric acid digests of the intestinal tissue, the kidneys, and the livers of the fish were determined by flame atomic absorption (Varian-Tectron model AA5) (Fletcher and King 1978).

Finally, the effect of intravenous injections of 20–25% of the total body zinc of the fish (as $ZnCl_2$, based on a whole body concentration of 15 μg Zn^{2+}/g wet wt) or of a saline solution (1% NaCl) on in situ Zn^{2+} uptake was examined from 1 d to 5 mo after the injections.

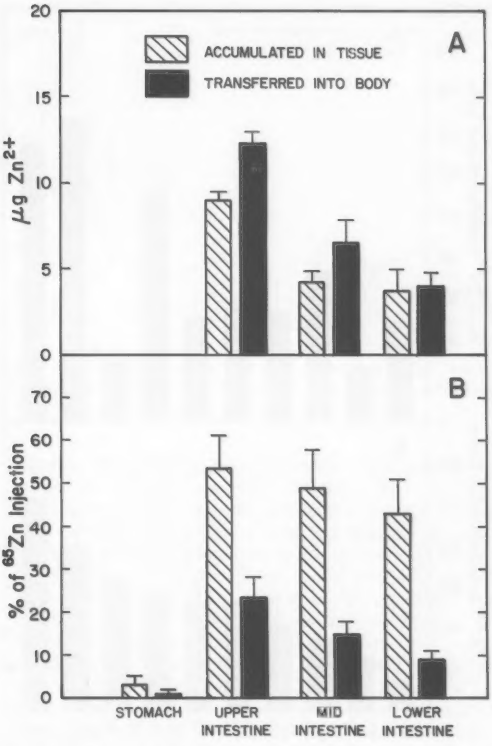

FIG. 1. The uptake of (A) ^{65}Zn plus a load of Zn^{2+} (50 μg) ($n = 7$) and (B) ^{65}Zn ($n = 5$) by different segments of the digestive tract. Values plotted are $\bar{x} \pm$ SE.

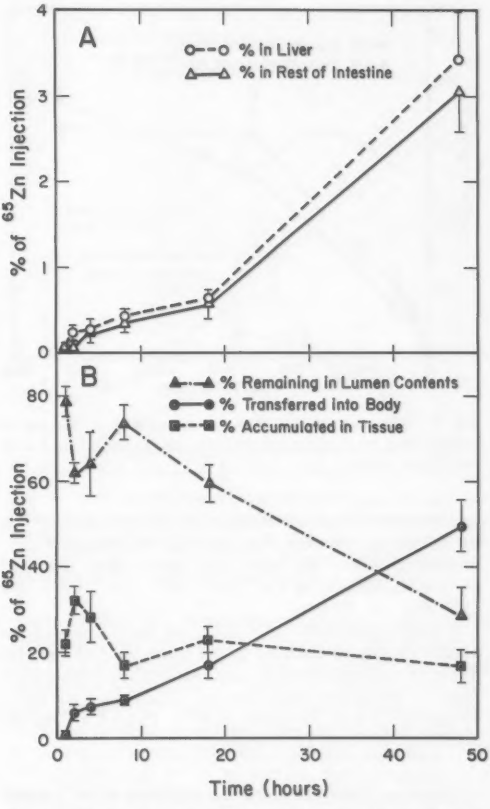

FIG. 2. (A) Accumulation of ^{65}Zn by the liver and intestine from a ligated portion of the upper intestine. (B) Time course of ^{65}Zn accumulation by the intestine and its transfer into the body from a ligated upper portion of the digestive tract (see Fig. 2A). Values plotted are $\bar{x} \pm$ SE ($n = 5-7$ per group).

Results

Site of Uptake

The amount of ^{65}Zn accumulated by the gastrointestinal tract tissue and transferred into the body was considerably greater in intestinal areas than in the stomach. The amount of ^{65}Zn and Zn^{2+} accumulated by and transferred across the tract declined from the upper to the lower intestine (Fig. 1A, B).

Factors Affecting Uptake

Time — The upper intestinal tissue accumulated approximately 20% of the ^{65}Zn injection within the 1st h. This proportion remained essentially the same throughout the period of observation (48 h) (Fig. 2B). Very little ^{65}Zn was transferred into the body in the first hour of exposure (i.e. no ^{65}Zn was transferred in three of the six fish examined). Thereafter, the amount of ^{65}Zn transferred from the intestinal tract to the rest of the body increased in a linear fashion (Fig. 2B). This was reflected by the percentage of injected ^{65}Zn appearing in the rest of the intestinal tract and in the liver (Fig. 2A).

Zn^{2+} load — When loads of 5–530 μg of Zn^{2+} were injected into the upper intestine, both the amount of zinc accumulated in the tissue and the amount transferred into the body increased with increasing loads (Fig. 3). While the relationship between the amount of Zn^{2+} in the lumen and the amount transferred into the body was not linear, saturation did not appear to have been reached at the highest load tested. When data from all loads were combined ($n = 54$), statistical analysis revealed that the amount of Zn^{2+} transferred into the body was directly proportional to the amount of Zn^{2+} accumulated in the intestinal tissue. The regression line ($r = 0.93$) can be expressed by the equation $y = 0.96x - 0.88$, where y = micrograms of Zn^{2+} transferred into the body and x = micrograms of Zn^{2+} accumulated in the tissue.

Other metals — Loads (200 μg) of Cu^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}, Hg^{2+}, Co^{2+}, and Cd^{2+} significantly ($P < 0.05$, lsd

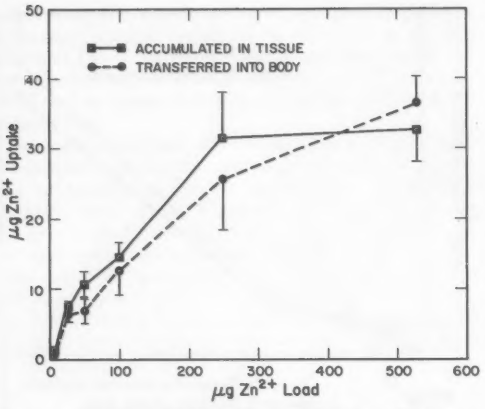

FIG. 3. The effect of Zn^{2+} loads on accumulation of ^{65}Zn and its transfer from the intestine into the body. Values plotted are $\bar{x} \pm$ SE ($n = 5$ per group).

test) depressed tissue accumulation of a 5-μg load of Zn^{2+} in the ligated upper portion of the intestine. The amount of Zn^{2+} transferred across the tract was significantly depressed ($P < 0.05$, lsd test) by Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, Cd^{2+}, and Cr^{2+} (Fig. 4A, B).

Copper significantly ($P < 0.05$, lsd test) depressed the amount of zinc accumulated by the tissue (by 33%) and the amount transferred across the intestinal wall (by 57%) at Cu^{2+} loads as low as five times the Zn^{2+} load (i.e. 5 μg Zn^{2+}, 25 μg Cu^{2+}) (Fig. 5). Loads of 10 or 15 μg Cu^{2+} had no significant effect on Zn^{2+} uptake.

Season — There was a seasonal difference in Zn^{2+} uptake from the gastrointestinal tract. Both the amount of Zn^{2+} accumulated in the tissue and transferred into the body from the ligated upper intestine peaked during the summer months (Fig. 6B). Feeding activity, as evidenced by the presence of food material in the digestive tract of at least one fish sampled from the field, was initiated in April and terminated in November. The amount of food material in the gut (expressed as a percentage of the body weight) reached a maximum in July, remained high in August, and fell off by September (Fig. 6A).

Level of zinc in the diet — There was no significant difference between either the tissue accumulation or the transfer into the body of a test dose of Zn^{2+} (52 μg) in two groups of fish fed a control or high-Zn^{2+} diet (60 vs 600 μg/g wet wt) (Table 1). As well, the Zn^{2+} concentrations of the intestine, kidney, and liver were not significantly different in fish fed the two diets. It should be noted that three of the control fish ($n = 11$) and four of the experimental group ($n = 12$) had lost weight by the termination of the study. However, weight loss or gain did not consistently influence Zn^{2+} uptake in fish from either group. Also, there were no differences in the Zn^{2+} uptake attributable to the sex of the fish.

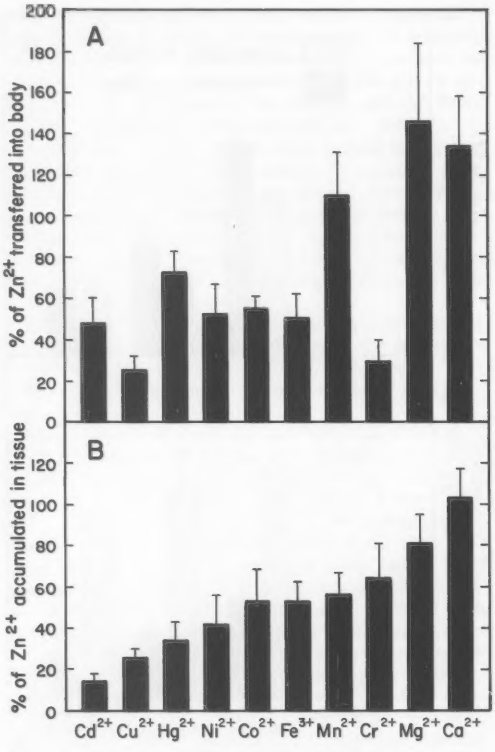

FIG. 4. The effects of metal loads on the accumulation of Zn^{2+} by the intestine and on its transfer into the body. The percentage of Zn^{2+} accumulated or transferred = [Zn^{2+} (load)/Zn^{2+} (no load)] × 100, where Zn^{2+} (load) is the amount of Zn^{2+} accumulated or transferred in the presence of a 200-μg metal load and Zn^{2+} (no load) is the amount of Zn^{2+} accumulated or transferred in the absence of the metal load. Values plotted are $\bar{x} \pm$ SE ($n = 5$–15 for each metal tested).

Body load — When the winter flounder were given an intravenous injection of Zn^{2+}, the intestinal levels of Zn^{2+} reached a peak within 7–11 d (Fig. 7).

Although the concentration of Zn^{2+} in the intestine was significantly higher in Zn^{2+}-injected fish than it was in the controls, the uptake of Zn^{2+} and ^{65}Zn by the ligated part of the intestine did not differ between the two groups (Table 2). No significant difference in the Zn^{2+} uptake by the intestine was observed between controls and Zn^{2+}-injected fish when examined from 1 d to 5 mo following the injections.

Discussion

The gastrointestinal tract of winter flounder is similar to that of other vertebrates in comprising a foregut (oesophagus and stomach), a midgut (intestine), and a hindgut (rectum) (Barrington 1957). In the present study, Zn^{2+} appeared to be taken up more readily from the uppermost portion of the

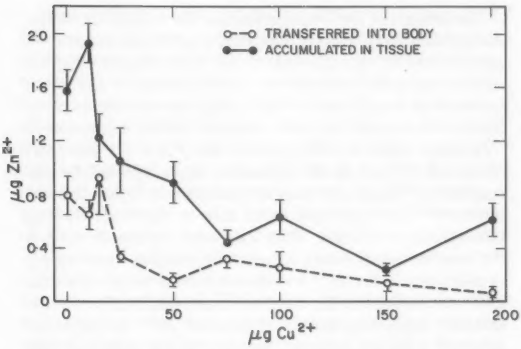

FIG. 5. The effects of Cu^{2+} on the accumulation of Zn^{2+} by the intestine and on its transfer into the body. Values plotted are $\bar{x} \pm$ SE ($n = 5$ per group).

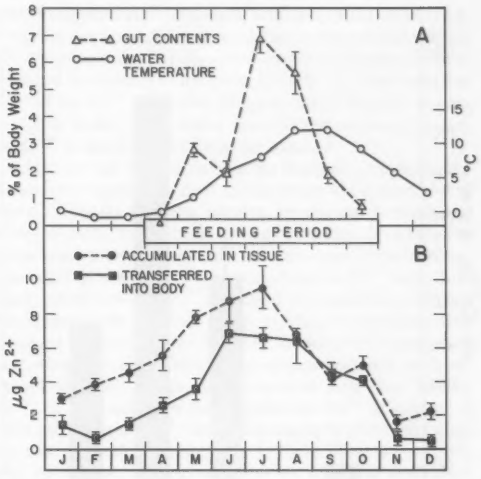

FIG. 6. (A) Seasonal change in gut content weight. (B) Seasonal change in accumulation of Zn^{2+} in the intestine and in its transfer into the body. Values plotted are $\bar{x} \pm$ SE. There were no differences in Zn^{2+} uptake in the 2 yr examined; therefore, monthly data were consolidated. Four to 19 fish were tested each month.

intestine. These findings are in agreement with a study carried out on rats by Van Campen and Mitchell (1965). ^{65}Zn was taken up more rapidly from the duodenum of the rat than from other sections; very little was absorbed from the stomach. While there is little information in the literature on sites of metal uptake in the gastrointestinal tract of fish, absorption of other substances has been found to be site dependent. For example, using an in situ perfusion method, Bogé et al. (1979) found that glycine uptake in rainbow trout (*Salmo gairdneri*) was linear in the upper intestine and a saturable phenomenon in the lower intestine. The major criticism of the in situ method is that it does not take into account the rate of passage of the ingesta. The rate of Zn^{2+} uptake may be higher at the upper end of the intestine, but if the ingesta spends less time in this region, the actual uptake may be greater in lower regions. Pentreath (1976) examined the tissue distribution of ^{65}Zn in the stomach, upper and lower intestine, and rectum of young plaice (*Pleuronectes platessa*) following feeding of radiolabeled *Nereis*. On a concentration basis, the highest activity of ^{65}Zn was found in the lower intestine; on a percentage basis, due to differences in tissue weight, the greatest proportion of ^{65}Zn was associated with the upper intestine (47%).

It appears that at least two steps are involved in the uptake of Zn^{2+} from the upper intestine of the flounder: accumulation of Zn^{2+} in the tissue and transfer into the body. The initial accumulation of Zn^{2+} in the intestinal tissue appeared to occur rapidly, but very little Zn^{2+} was transferred into the body in the 1st h of exposure. Thereafter, the amount transferred increased at a linear rate. A similar two-step absorption process, in which Zn^{2+} transfer into the blood follows an obligatory accumulation in the intestinal tissue, has been hypothesized to occur in rats (Sahagian et al. 1966; Kowarski et al. 1974; Smith et al. 1978). In addition, there appears to be a second, more rapid process in rats, whereby Zn^{2+} is transferred into the body within minutes of contact with the mucosal tissue, i.e. without any appreciable binding to the mucosal tissue (Davies 1980; Jackson et al. 1981).

When different loads of Zn^{2+} were instilled into the intestinal lumen of the flounder the proportion of Zn^{2+} accumulated in the intestinal tissue was greater from lower than from higher doses. This implies that the first step in Zn^{2+} absorption in the flounder involves binding to specific sites on or within the intestinal cells. In situ studies indicated that Zn^{2+} accumulation by the intestinal tissue of mice involved binding

TABLE 1. The effects of a high Zn^{2+} diet on the uptake of Zn^{2+} from the upper intestine of the winter flounder. Control diet (Zn^{2+} = 60 μg/g wet wt); high-Zn^{2+} diet (Zn^{2+} 600 μg/g wet wt). Values expressed as $\bar{x} \pm$ SE (n = number of fish).

Diet	n	Zn^{2+} accumulated in the intestinal tissue (μg)	Zn^{2+} transferred into the body (μg)	Sex	n	Zn^{2+} concentration (μg/g dry wt) Intestine	Kidney	Liver
Control	11	5.41±0.21	6.47±1.84	Male	5	99.9±3.67	161.0±12.5	128.0±18.7
				Female	3	96.0±2.33	127.4±4.25	131.0±7.36
High Zn^{2+}	12	5.61±0.59	6.72±1.22	Male	7	103.0±2.08	197.0±16.5	108.0±8.06
				Female	5	102.0±4.94	152.0±9.38	170.0±27.7
P		NS	NS			NS	NS	NS

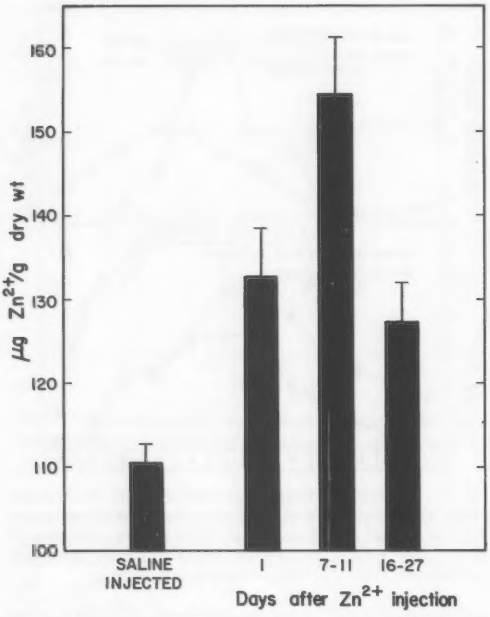

FIG. 7. Changes in intestinal Zn^{2+} concentration following Zn^{2+} injections. Values plotted are $\bar{x} \pm$ SE. The number of saline-injected fish examined = 34. The number of Zn^{2+}-injected fish examined after 1 d = 6, after 7–11 d = 14, and after 16–27 d = 14.

to specific sites within the mucosa (Hamilton et al. 1978). In rats, Zn^{2+} appeared to bind to specific sites at low doses (1–50 µg), but nonspecific binding was apparent at higher doses (50–200 µg) (Davies 1980).

The amount of Zn^{2+} transferred into the body of the flounder appeared to be directly proportional to the amount of Zn^{2+} accumulated by the intestinal tissue. This suggests that the second step in Zn^{2+} absorption, i.e. the transfer of Zn^{2+} from the mucosal tissue into the blood, may be a passive process. Such a mechanism has been proposed for the absorption of ^{65}Zn from water via the gills of the plaice (*P. platessa*) (Pentreath 1973*a*). In this instance it was suggested that adsorption of ^{65}Zn to gill mucous resulted in a higher concentration of ^{65}Zn in the gill tissue than in the blood flowing through the gill lamellae. Thus, Zn^{2+} could be transferred into the blood stream down a concentration gradient. By contrast, in rats a plot of the Zn^{2+} transferred into the body versus the Zn^{2+} accumulated in the intestinal tissue exhibited saturation kinetics, suggesting that the release of Zn^{2+} to the blood involved a carrier-mediated process, which would be rate limiting at high concentrations of Zn^{2+} in the intestinal tissue (Davies 1980).

The level of Zn^{2+} in the lumen appears to be an important determinant of the extent of Zn^{2+} absorption in the flounder. Although the proportion of Zn^{2+} absorbed declined as the intraluminal Zn^{2+} load increased, the amount of Zn^{2+} absorbed actually increased with increasing loads over a fairly wide range (5–250 µg). Based on these in situ findings the potential exists for flounder to take up increasing amounts of Zn^{2+} if the Zn^{2+} level in their diet (or in sediments ingested with the diet) increases. The proportion of Zn^{2+} absorbed from the diet of rats also declined as the amount of Zn^{2+} increased, but Jackson et al. (1981) suggested that under normal dietary conditions the absorptive mechanism operated in the linear portion of the curve. In other words, a rise in the Zn^{2+} content of the diet resulted in a proportionate rise in the amount of Zn^{2+} absorbed. Similarly, Miller (1970) found in ruminants that although the percentage of dietary Zn^{2+} absorbed from the diet declined with increasing levels of Zn^{2+} in the food, the total amount of Zn^{2+} absorbed actually increased.

TABLE 2. The effects of intravenous Zn^{2+} injections on the uptake of (A) ^{65}Zn and (B) ^{65}Zn plus Zn^{2+} by the intestine. Winter flounder were injected intravenously with saline or Zn^{2+} equivalent to 25% of their total body Zn^{2+}. Seven days following the injection the upper portion of the intestine was ligated in situ. ^{65}Zn (A) and ^{65}Zn plus a load of stable Zn^{2+} (52 µg) (B) were injected into the ligated segment for an exposure period of 9–10 h. The intestinal Zn^{2+} concentration was analyzed in the unligated portion of the intestine. Values expressed as $\bar{x} \pm$ SE (n = number of fish).

(A)

Treatment	n	^{65}Zn accumulated (%)	^{65}Zn transferred (%)	Intestinal Zn^{2+} (µg/g dry wt)
Zn^{2+} injected	10	43.0±5.75	19.9±2.59	152.0±5.11
Saline injected	8	47.5±4.59	20.1±3.13	127.0±2.98
P		NS	NS	<0.01

(B)

Treatment	n	Zn^{2+} accumulated (µg)	Zn^{2+} transferred (µg)	Intestinal Zn^{2+} (µg/g dry wt)
Zn^{2+} injected	10	9.12±0.75	17.4±1.95	151.0±5.22
Saline injected	11	7.70±0.73	18.4±1.18	128.0±3.43
P		NS	NS	<0.01

Several metals exerted an inhibitory effect on the amount of Zn^{2+} accumulated in the intestinal tissue of the flounder and on its transfer into the body. Based on an equilibrium dialysis technique, Cu^{2+} was the only metal that interfered with Zn^{2+} binding to the mucosal cytosol proteins in the winter flounder (Shears and Fletcher 1979). In view of this, the inhibitory effect exerted by the other metals on in situ uptake of Zn^{2+} may be mediated at the surface of the mucosal cells. Cu^{2+} may also interfere with the transfer step, i.e. from "binding protein(s)" to the blood. Cu^{2+} also competed with the binding of Zn^{2+} to winter flounder plasma (Fletcher and Fletcher 1978). Van Campen (1969) found that in situ injections of Cu^{2+} into the duodenal segment of the rat intestine interfered with the absorption of ^{65}Zn. In situ investigations in mice indicated that there may also be analogous binding sites for uptake of iron and zinc (Hamilton et al. 1978). As well, addition of Cd^{2+} to the diet reduced the amount of Zn^{2+} absorbed by ruminants (Hiers et al. 1967). Therefore, the potential exists for elevated levels of several heavy metals to interfere with fish obtaining their required Zn^{2+}.

Based on the in situ seasonal uptake, the capacity of the flounder to take up Zn^{2+} from the digestive tract is greatest during the summer months. This coincides with the feeding period, when presumably the zinc required for normal growth must be obtained. The ambient water temperature also reached a maximum value during this period, but uptake of Zn^{2+} is probably not directly controlled by temperature. Zn^{2+} uptake began to decline in September when the water temperature was still at its peak.

Feeding the flounder an increased level of Zn^{2+} in the diet (600 vs 60 μg/g wet wt) for 5 wk did not result in a significant increase in the Zn^{2+} concentration of kidney, liver, or intestinal tissue. If the Zn^{2+} in the diet was available for absorption, one would expect that more Zn^{2+} would have been absorbed from the diet with the added Zn^{2+} than from the control diet. Since there appears to be no decrease in the Zn^{2+} absorptive capacity of the flounder fed a high Zn^{2+} diet, it would appear that regulation of tissue Zn^{2+} levels may have been achieved by elimination of the extra Zn^{2+} absorbed. In mammals there is some species variation in the extent of tissue elevation observed when excess Zn^{2+} is fed. Regulatory mechanisms apparently break down in calves when they are presented with high levels of dietary Zn^{2+}. When 600 μg/g Zn^{2+} was added to the diet for 21 d, the level of Zn^{2+} in the liver was elevated 500% above control levels (Kincaid et al. 1975). Tissue levels were not significantly elevated in rats fed diets containing 600 μg/g Zn^{2+} (Ansari et al. 1975) but Zn^{2+} did begin to accumulate in rat liver and kidney when diets containing 1000 μg/g or higher were fed (Chen et al. 1977). Concentrations of Zn^{2+} in different species of fish appear to be related to factors other than their feeding habits. Ting (1971) did not observe any significant differences in the Zn^{2+} concentrations of seven species of fish comprising four different feeding habits. On the other hand, there are reports of species of fish with similar feeding habits exhibiting significant differences in their whole body Zn^{2+} concentrations (Wiener and Giesey 1979; Cross et al. 1975; Milner 1979). In a laboratory study, Milner (1979) found that an increase in the dietary Zn^{2+} level of young plaice resulted in increased whole body concentration of Zn^{2+}. However, the percentage retention of ingested Zn^{2+} decreased with increasing input level, implying that some form of regulation was occurring. Milner (1979) thought that the regulation might be fortuitous due to a limited availability of the metal from the diet. He found that 60% of the Zn^{2+} in the diet (*Artemia salina* nauplii) was not available to the young plaice, possibly due to strong binding of Zn^{2+} to nondigestible cuticular material.

Elevating the level of Zn^{2+} in the flounder by injecting the fish intravenously with Zn^{2+} did not result in a lowering of in situ Zn^{2+} uptake from the intestine. In contrast, Richards and Cousins (1975) found that intestinal absorption (defined as the percentage of an oral dose of ^{65}Zn transferred to the carcass) was reduced when rats were injected with a Zn^{2+} load. Similarly, injections of Zn^{2+} decreased the percentage of ^{65}Zn transferred to the vascular perfusate when rat intestines were perfused in situ (Smith et al. 1978). Cousins (1979) proposed that when the zinc status of an animal becomes elevated, metallothionein, a high cysteine protein capable of binding Zn^{2+}, is synthesized in the intestine and Zn^{2+} absorption is reduced, the bound Zn^{2+} being subsequently eliminated when the mucosal cells are sloughed off. Preliminary investigation (M. A. Shears, unpublished data) has indicated that metallothionein is also present in the flounder intestine following intravenous injections of Zn^{2+}. However, unlike mammals, Zn^{2+} uptake was not inhibited, indicating a possible difference in homeostatic control mechanisms in fish. In a marine fish such as the winter flounder, which has a fixed feeding period in which to obtain its required Zn^{2+}, uptake of Zn^{2+} from the gastrointestinal tract may not be limited by the Zn^{2+} status of the animal in the same manner as is observed for mammals (Cousins 1979). Rather, the uptake of Zn^{2+} may be maximized as is indicated by the increases in in situ Zn^{2+} uptake observed when increasing loads of Zn^{2+} were present in the intestinal lumen. This might be expected if the availability of Zn^{2+} from the diet is already limited by factors such as an excess of other metals, as is indicated by the present in situ findings, or by the binding of Zn^{2+} to nondigestible material, as suggested by Milner's (1979) study.

In the event of exposure to elevated dietary levels of Zn^{2+}, the present study indicates that elimination mechanisms may play a greater role than limitation of gastrointestinal uptake in maintaining Zn^{2+} homeostasis in marine fish. The possible routes of Zn^{2+} elimination from marine organisms (i.e. kidney, gills, gastrointestinal tract, or across the body surface) have been reviewed by Coombs (1979) and Bryan (1979). The relative importance of each of these routes of elimination has not been determined in fish; in view of the role that elimination may play in Zn^{2+} homeostasis, this is an area requiring further investigation.

Acknowledgments

We thank Joanne Embree and Madonna Whiteway for help in conducting the experiments. This research was supported by National Research Council of Canada contract No. 031-531 and Natural Sciences and Engineering Research Council of Canada grant No. A6836. MSRL contribution No. 453.

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Heavy Metals in Tissues and Organs of the Narwhal (*Monodon monoceros*)[1]

R. WAGEMANN

Freshwater Institute, 501 University Crescent, Winnipeg, Man. R3T 2N6

N. B. SNOW

Petro Canada, P.O. Box 2844, Calgary, Alta. T2P 3E3

AND A. LUTZ AND D. P. SCOTT

Freshwater Institute, 501 University Crescent, Winnipeg, Man. R3T 2N6

WAGEMANN, R., N. B. SNOW, A. LUTZ, AND D. P. SCOTT. 1983. Heavy metals in tissues and organs of the narwhal (*Monodon monoceros*). Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 206–214.

Sixty narwhals (*Monodon monoceros*) were sampled in the vicinity of Pond Inlet, N.W.T., during the summer of 1978 and 1979. Concentrations of Pb, Cu, Cd, Hg, Se, As, and Zn were measured in liver, kidney, muscle, and blubber. All elements except As were lowest in concentration in the blubber and highest in kidney and liver; Cd and Zn were generally higher in kidney than in liver, while the converse was true for Pb, Cu, and Hg. Cadmium levels in liver and kidney had high interanimal variability but were generally higher than would be expected based on existing marine mammal Cd content data. Certain metals were correlated with animal size and sex. Mercury in kidney, muscle, and blubber and Cd in muscle appear to accumulate during growth. A number of interelement associations with extremely high probabilities were found: among them, that between Hg and Se and Cd and Zn in liver and kidney tissues. The latter association is thought to be related to the presence of metallothionein. The data presented are discussed in terms of what little is known of the biology of the narwhal and represent a baseline for a resource organism which is harvested in an area already subject to mining activity, the level of which is due to increase in the future.

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Soixante narvals (*Monodon monoceros*) ont été échantillonnés dans le voisinage de l'inlet Pond (T.N.-O.) pendant les étés 1978 et 1979. Les concentrations de Pb, Cu, Cd, Hg, Se, As et Zn ont été mesurées dans le foie, le rein, le muscle et la graisse. La concentration de tous les éléments, à l'exception de l'As, est minimale dans la graisse et maximale dans le rein et le foie; le Cd et le Zn sont généralement plus élevés dans le rein que dans le foie, tandis que c'est l'inverse pour le Pb, le Cu et le Hg. Il y a forte variation, d'un animal à l'autre, des niveaux de Cd dans le foie et le rein, mais ces niveaux sont généralement plus élevés qu'on pourrait le croire en se fondant sur les données actuelles sur le Cd des mammifères marins. Il y a corrélation entre certains métaux et la taille et le sexe de l'animal. Le Hg dans le rein, le muscle et la graisse, ainsi que le Cd dans le muscle, semblent s'accumuler durant la croissance. On a découvert plusieurs associations inter-éléments, avec très hautes probabilités, parmi lesquelles celles du Hg et du Se, et du Cd et du Zn dans les tissus hépatiques et rénaux. On croit que cette dernière association est liée à la présence de métallothionéine. Nous analysons les données à la lumière de nos connaissances incomplètes de la biologie du narval. Ce sont des données de référence fondamentales sur une ressource récoltée dans une région où se poursuivent déjà des activités minières, dont le niveau ira en augmentant.

Received March 19, 1982
Accepted October 20, 1982

Reçu le 19 mars 1982
Accepté le 20 octobre 1982

ALTHOUGH the major global pathway for transport of heavy metals (with the exception of Pb) is water, very little transport occurs beyond coastal areas (Beijer and Jernelov 1978). The concentration of heavy metals in oceans is generally very low

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6864)
Imprimé au Canada (J6864)

(Smith 1974). Nevertheless, most marine organisms tend to accumulate heavy metals; i.e. they have metal concentrations higher than in the medium in which they live. This is as true for nonessential metals (e.g. Cd and Hg) as for essential ones (e.g. Zn). Even a slight elevation in the concentration of heavy metals above background levels can expose marine organisms to conditions that they may not normally encounter, which may be reflected in increased metal burdens in their tissues and organs, should the animals spend considerable time in such an environment.

The potential impact of contamination of aquatic habitats in the Arctic on the rate of accumulation of metals in biota has been recognized for some time. A correlation between man-induced contamination of aquatic habitats in the Arctic and increased metal burdens has been reported (increased Pb and Zn in sedentary organisms and seaweed (Fallis 1982); increased Pb in the spotted wolffish, *Anarhicas minor* (Bollingberg and Johansen 1979)). High metal burdens in animals from a seemingly pristine area in the Arctic have also been reported (Hg in ringed seal) (Smith and Armstrong 1975). The separation of metal burdens in marine biota, particularly for migratory animals, into natural and anthropogenic components is not a simple procedure and requires initially an adequate data base for metal burdens in Arctic animals. Knowledge of the norms of metal burdens in marine mammals and the factors that affect such norms is deeply connected with an understanding of the term "pollution" and is essential for enlightened and rational management of resource organisms and their coastal habitats.

Heavy metal concentration data for marine lower trophic level organisms are widely scattered and relatively sparse in the literature (Bryan 1976; Fallis 1982). Comparable data for marine mammals are even scarcer, and there are none published to date for narwhal (*Monodon monoceros*). In this paper, we present baseline data for heavy metals, and other elements associated with mining activities, in tissues and organs of the narwhal. This small, toothed whale is a renewable resource harvested by Canadian Inuit. It is an ill-understood marine mammal which is migratory. Part of its life cycle is spent in the vicinity of operating mines in the eastern Arctic, and it is also harvested in the same localities by Inuit during the spring and summer months.

Materials and Methods

Sampling Procedure

All samples were collected from narwhals killed by Inuit hunters from the settlement of Pond Inlet, northern Baffin Island (72.6°N, 78.4°W). The kills were part of the annual subsistence hunt, and our sampling was therefore carried out on an opportunistic basis.

Liver samples were usually cut from the lower end of the lobe. Muscle was taken from the dorsal side at the midpoint of the whale or along the ventral surface near the ribs. Blubber was taken from the chin just behind the jaw or from the ventral midline. Kidney samples were cut from various areas of the organ. The tissue samples were put into plastic bags and stored on ice until deep-frozen later. The interval between collection and freezing was in most cases 1−3 h, but up to 5 d in a few cases. Once frozen, the samples were maintained in that state until thawed for analysis.

Analytical Procedures

Tissue samples of liver, kidney, and muscle (10−100 g wet wt) were weighed accurately before and after drying. Complete thawing of samples and possible loss of moisture was avoided by keeping samples, up to the time of weighing, in a refrigerator after removal from the −60°C freezer. Samples were dried in acid-washed glass petri dishes at 80°C overnight (16 h) in a convection oven. It was experimentally verified that the drying process did not cause any significant loss of Hg. Moisture was not determined in blubber that was analysed "as received."

Dried, ground (IKA micromill with stainless steel blade and cup) tissue samples (1−2 g) were digested first with concentrated nitric acid, evaporated nearly to dryness, and then heated to charring with a 1-mL mixture of sulfuric and nitric acids (4:1) after which the solutions were clarified by heating with 50% hydrogen peroxide (Analytical Methods Committee 1976). Analyses for Cu, Zn, and Cd were then performed with a Varian AA5 (with BC 6 background corrector) flame spectrophotometer using an air−acetylene flame. Where concentrations were low (e.g. muscle) the metals were chelated and extracted with diethylammonium-diethyldithiocarbamate (DDDC) dissolved in *n*-butyl acetate (0.5%) to concentrate the metals and enhance the signal. Lead was determined by flameless atomic absorption spectrophotometry (AAS) using a model 90 carbon rod attachment. Solutions were preconcentrated (i.e. extracted with DDDC in *n*-butyl acetate), followed by evaporation and destruction of the remaining complex with concentrated nitric acid prior to analysis.

For Hg analyses, all tissues were digested with a mixture of sulfuric and nitric acids (4:1) at 70°C, followed by complete destruction of organic matter with potassium permanganate (6%). Measurements of Hg were made by the flameless AAS method of Armstrong and Uthe (1971).

All tissues were digested for Se assay with a mixture of nitric and perchloric acids (4:1) at approximately 200°C with subsequent addition of hydrochloric acid to 30% acid concentration. Additional nitric acid was necessary for complete destruction of blubber tissue. Essentially, the semiautomated hydride method of Vijan and Wood (1974) was followed to measure Se.

Approximately 10 g of blubber was digested with fuming nitric acid (90%), heated to charring with concentrated sulfuric acid, and clarified with hydrogen peroxide (50%). The initial addition of acid requires extreme care because of the violent exothermic reaction. Finally, perchloric acid was added and heated until SO_3 fumes evolved. The solution was then cooled, made to volume with double-distilled water, and analysed for Pb, Cu, Cd, and Zn by anodic stripping voltametry using a Princeton Applied Research model 374 polarograph with a 303 SMD electrode.

Seawater (Strathcona Sound) was analysed for Cu, Pb, Zn, and Cd by anodic stripping voltametry using a Princeton Applied Research model 174 polarograph. Arsenic was coprecipitated with thionalide (Portmann and Riley 1964),

followed by digestion and determination by the semi-automated borohydride method of Vijan and Wood (1974). Total Fe was determined colorimetrically using the *o*-phenanthroline method of Armstrong (1957).

Statistical Treatment

For each tissue, multilinear regressions (MLR) were performed on all elements measured except As (Pb, Cu, Cd, Hg, Se, and Zn,) as well as lengths of animals and tissue moisture. Concentrations based on dry weight of tissue, and length in centimetres, were used in these regressions. Multiple linear regression analyses were carried out using the following basic model:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_p X_p + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \ldots + \beta_{1_p} X_1 X_p$$

where X_1 = sex (coded 1 for females, 0 for males), X_2 = length, X_3 = moisture proportion, X_4 = Hg concentration, X_5 = Se concentration, X_6 = Cd concentration, X_7 = Cu concentration, X_8 = Zn concentration, and X_9 = Pb concentration. The model can be factored as follows:

$$Y = \beta_0 + \beta_1 X_1 + (\beta_2 + \beta_{12} X_1) X_2 + (\beta_3 + \beta_{13} X_1) X_3 + \ldots$$

The second term within the parentheses vanishes whenever $X_1 = 0$ (i.e. for males), the overall coefficient for $X_2, X_3, \ldots$ being $\beta_2, \beta_3, \ldots$, respectively. When $X_1 = 1$ (i.e. for females), the overall coefficient for $X_2, X_3, \ldots$ becomes the respective sums of $\beta_2 + \beta_{12}, \beta_3 + \beta_{13}, \ldots$ The procedure is mathematically identical to analysis of multiple covariance for between-groups comparisons of both slopes and levels when only two groups are being compared. Significance of the various β_i values indicates differences in level between the sexes, whereas significance of the β_{ij} values indicates differences in the respective partial (=bivariate) slopes.

A critical probability level of 0.9 was chosen for retention of any variable in the backward stepwise fitting procedure used to indicate not only close associations but also those which were not very good. Probability levels are classed herein as $0\rightarrow$ ($P < 0.9$), $1\rightarrow$ ($0.9 \leq P < 0.99$), $2\rightarrow$ ($0.99 \leq P < 0.999$), and $3\rightarrow$ ($0.999 \leq P$).

In addition, since there appeared to be some measure of positive means−variance correlation, and there is some indication in the literature (Scott and Armstrong 1972; Scott 1974) that such correlations are common in contamination relationships, two versions of the model were fitted, i.e. a simple, untransformed model and a model with all variables except sex (X_1) $\log_{10}$-transformed. The models were fitted sequentially with each of the metallic elements as predictand and sex, length, moisture, and the other elements as predictors. Moisture was also treated as a predictand, since at least one of the elements, Hg, is a known powerful diuretic.

Results

The moisture content is somewhat different for different tissues. The conversion from a dry weight to a wet weight concentration basis therefore requires the following conversion factors: 0.281 for muscle, 0.257 for liver, and 0.213 for kidney.

Precision estimates (Table 1) were determined from repetitive analyses of a tissue sample which always included redigestion of a new subsample. A measure of accuracy of the analytical results was obtained by analysing a certified reference material (U.S. Bureau of Standards, bovine liver, No. 1577). The difference between determined and certified values was not significant for any element at the $\alpha = 0.05$ level. Further confirmation of the reliability of the data was obtained through comparison of analyses with another laboratory (National Research Council of Canada, Ottawa, Ont.). The agreement was considered to be quite good.

Trace metal concentrations in Strathcona Sound water are for the most part comparable with oceanic levels (Table 2), although surface concentrations (i.e. in water immediately under the ice) were consistently higher (except for As) than at lower depths.

The standard deviations associated with the average metal concentrations in tissues (Table 3) do, it appears, reflect largely interanimal variations in concentration, since the contribution from analytical variation was relatively small (Table 1). The metal concentrations in blubber were, as expected, very low, and the standard deviations of the averages were largest for this tissue (except for Hg). Since no distinction in the data from dorsal or lower-jaw blubber samples was made, a contribution to variance from this source was possible. The lipid composition is reported to differ in lower-jaw and dorsal blubber of some cetaceans (Ackman and Eaton 1971; Litchfield et al. 1975), but whether metal concentrations vary concomitantly with changes in lipid composition is not known. Similarly, no distinction between epaxial and hypaxial muscle tissue was made, and how much this contributed to variance is also unknown.

The relative standard deviation is larger for Cd in each tissue than for other elements. This implies that the Cd concentration was greatly different in different animals. The Cd concentrations in kidneys from different animals appear to be bimodally distributed (Fig. 1), while the ages of animals are

TABLE 1. Analytical precision (coefficient of variation) for the determination of metals, As, and Se in different tissues of narwhal (data represent percentages).

	Pb	Cu	Cd	As	Zn	Hg	Se
Liver	6.7	2.0	1.1	1.3	1.6	1.9	7.2
Kidney	3.1	3.0	1.6	1.4	1.1	2.6	8.5[a]
Muscle	12[a]	1.6	4.8	0.4	1.4	5.6	5.5
Blubber	19	13	31	1.0	11	7.5	15

[a]Estimated from other work.

TABLE 2. Concentrations (micrograms per litre) of some trace elements in water of Strathcona Sound, northern Baffin Island, in comparison with oceanic concentrations.

Depth[a] (m)	η[b]	Zn	Cd	Pb	Cu	Fe	As
			Strathcona Sound water (1976)				
2	9	11.2	5.7	0.5	6.3	23.8	1.0
5	1	8.4	0.4	0.3	2.3	6.0	1.0
10	8	2.8	0.2	<0.1	1.8	9.4	1.0
15	1	3.8	0.2	<0.1	2.2	4.8	4.8
20	8	1.9	0.3	0.2	1.6	7.6	0.9
30	6	1.2	0.1	0.4	2.2	15.6	0.9
50	5	1.4	0.1	<0.1	1.6	3.6	1.0
75	5	1.4	<0.1	<0.1	2.0	8.9	0.9
100	4	1.7	0.1	<0.1	1.7	4.0	0.9
150	3	1.3	0.1	<0.1	2.3	24.9	1.1
200	3	2.4	<0.1	<0.1	2.0	11.2	1.0
250	1	1.9	0.1	6.0	2.0	18	0.9
				Ocean water[c]			
		2.0–12.3	0.11	0.05	0.2–2.0	0.2–6.6	0.2–4.0

[a]Measured from the top surface of the ice which was 2 m thick.
[b]Number of stations averaged.
[c]From Smith 1974.

unimodally distributed (Fig. 2). Our sample of 60 animals may therefore have consisted of two different groups of animals that had lived in two distinct environments as far as the Cd concentration was concerned.

As expected, metal concentrations were highest in liver with the exception of Zn and Cd, which were consistently higher in the kidney than in the liver. All metals and Se were higher in muscle than in blubber. Mercury yielded the highest muscle to blubber ratio and Pb the lowest although it was still larger than 1. The atomic concentration ratio Hg/Se was calculated for the four tissues. For liver, this ratio ranged from 0.22 to 1.7 with a mean value of 0.59 (as calculated from the average Hg and Se concentrations in this tissue) (Table 3); for kidney, from 0.066 to 0.56 with a mean of 0.21; for muscle, from 0.23 to 1.37 with a mean of 0.75, and for blubber, from 0.039 to 1.4 with a mean of 0.15.

The results of MLR analyses for narwhal muscle, kidney, liver, and blubber are presented in Table 4. Unfortunately, not all variable data were available for all specimens and tissues. In addition, neither moisture nor lead was measured for an adequate number of blubber specimens.

In comparing the untransformed and transformed goodness-of-fit of the models (i.e. by means of final coefficients of determination, R^2), 13 transformed versions were considerably higher than untransformed, 3 were approximately equal, and 10 were somewhat poorer. We have chosen to report only the results of the MLR analyses on transformed data.

Few of the analyses showed significant differences in level between the sexes (7 of 26), whereas 22 of 26 showed at least one difference in partial slope of the predictand on predictor; however, only 7 of these showed a consistent difference in slope (i.e. irrespective of whether the variable was the predictand or predictor). There appears to be no obvious pattern to the differences.

As a predictor, length appears in 17 final relationships, of which only 5 are highly significant ($P > 0.99$), namely, with Cd in liver and muscle, and with Hg in muscle, kidney, and blubber (the latter having probabilities far beyond 0.999). All of these relationships, except that with Cd in the liver, are positively related, which is in accordance with the known extremely slow clearance of Hg from such tissues. Length is also positively and consistently (i.e. same direction of partial slopes for both sexes) associated with Cd in the kidney, although somewhat less strongly than in liver and muscle. In liver, Hg appears to be an anomaly in that females show a negative relationship, whereas males conform to the rest of the tissues. We have no explanation for this.

Moisture appeared to be somewhat related to metal concentration in 8 of the 18 possible relationships for the three tissues (moisture was not measured in blubber). A consistent association between moisture and metal concentration (i.e. when moisture was used either as the dependent or independent variable) was found only for Se in liver, Cu in muscle, and Hg in kidney, but since these interactions were rather weak (except for Se in liver), moisture was not included in the tabulation of pertinent interactions.

With the exception of Pb, all the metals are extremely well predicted by the model in kidney, liver, and blubber and quite well in muscle. This latter finding fits quite well with general mammalian physiology in that general turnover rates are much higher in kidney and liver than in muscle. Thus, the latter tissue would tend to be an integrator of the animal's past history, whereas the other tissues would be more indicative of recent events. Blubber turnover is entirely unknown; in spite of this, all the final R^2 values are well beyond $P = 0.999$.

There are several very strong interrelationships that should be noted: (1) Hg–Se in both kidney and liver, although not

TABLE 3. Average (arithmetic) concentrations ($\bar{y}$) (micrograms per gram) and standard deviations (SD) of metals in narwhal tissues.

	Pb	Cu	Cd	Hg	Se	Zn	As
Liver							
$\bar{y}$ (dry wt)	0.109	20.6	133	23.8	15.8	151	1.27
SD	0.048	12.7	130	12.2	7.19	38.4	0.698
n	38	38	38	38	38	38	37
$\bar{y}$ (wet wt)	0.028	5.27	34.1	6.10	4.06	38.8	0.326
SD	0.012	3.26	33.3	3.12	1.84	9.85	0.179
Kidney							
$\bar{y}$ (dry wt)	0.082	11.0	298	8.05	14.8	193	1.61
SD	0.042	2.03	192	4.77	4.01	44.4	0.793
n	55	55	55	55	55	55	55
$\bar{y}$ (wet wt)	0.018	2.34	63.5	1.71	3.15	41.1	0.343
SD	0.009	0.43	41.0	1.01	0.85	9.45	0.169
Muscle							
$\bar{y}$ (dry wt)	0.031	2.35	0.69	3.00	1.57	63.1	0.576
SD	0.020	0.52	0.78	1.00	0.34	10.9	0.412
n	58	58	58	58	58	58	55
$\bar{y}$ (wet wt)	0.009	0.66	0.19	0.85	0.44	17.8	0.162
SD	0.006	0.15	0.22	0.28	0.10	3.06	0.116
Blubber							
$\bar{y}$ (wet wt)	0.016	0.077	0.078	0.027	0.071	1.12	2.93
SD	0.014	0.067	0.15	0.019	0.059	0.65	12.1
n	45	45	45	49	47	45	25

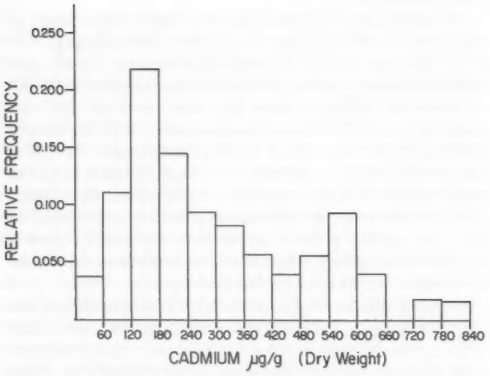

FIG. 1. Relative frequency of Cd concentrations in renal tissues of narwhal.

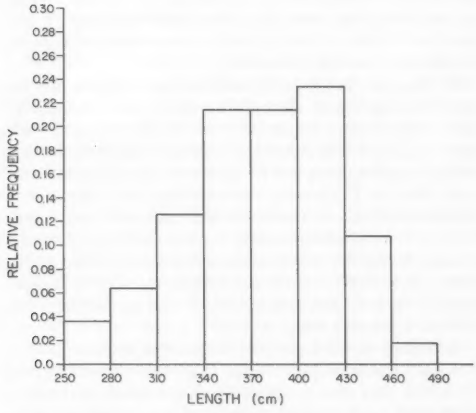

FIG. 2. Relative frequency of size of animals in a sample of 60 narwhals.

in either of the other tissues, (2) Zn−Cd in both kidney and liver, but not in the other tissues, (3) Zn−Cu in kidney and blubber, but one-way or nonexistent in the other tissues, (4) Pb−Cd in kidney, but one-way or nonexistent in other tissues, and (5) Hg−Cd in liver and blubber, but one-way or nonexistent in other tissues. Other strong relationships exist but tend to be one-way; i.e. in the final models, one element may be a strong predictor of the other, but the reciprocal is not true.

Amongst the various associations, those between Hg and Se and between Zn and Cd (in liver and kidney) are noteworthy because of the apparent antagonism between Se and Hg, and the isomorphism of Zn and Cd in a metalloprotein (metallothionein), much implicated in the detoxification mechanisms of heavy metals in mammals and fish.

Discussion

The average Hg concentration in narwhal liver (6.10 µg/g wet wt) is lower than the concentration in the same organ of some short-finned pilot whales (Stoneburner 1978) and higher than in minke whales (Johansen et al. 1980). Since the ages of the sampled animals are not known (and age is a governing factor), such a comparison can only be very approximate.

TABLE 4. Associations between variables (metals, Se, sex (SX), length (L)) and the dependent variable at $0.9 \leq P < 0.99$, at $0.99 \leq P < 0.999$ (underlined), and at $0.999 \leq P$ (doubly underlined) in various tissues of narwhal. The directions of female and male regression slopes are indicated by algebraic signs, the upper sign always referring to the female regression slopes. A zero indicates zero slope. One algebraic sign in front of a symbol indicates no significant difference between male and female regression slopes.

Dependent variable	Independent variables			
	Liver	Kidney	Muscle	Blubber
Hg	+SX, $\dot{-}$L, +Se, +Cd	$\dot{+}$L, +Se	−SX, +L, $\dot{+}_0$Zn	+L, +Cd, $\dot{+}_0$Zn
Se	−SX, $\dot{+}$L, $\dot{+}$Hg, $\dot{+}$Cd, $\dot{-}_0$Zn, +Pb	$\dot{-}_0$L, +Hg, $\dot{+}_0$Cd	+Hg, −Cd, +Cu, $\dot{+}_0$Zn	+Cd, +Zn
Cd	−L, $\dot{+}$Hg, $\dot{+}$Se, +Zn, $\dot{-}_0$Pb	$\dot{+}$L, −Hg, $\dot{+}_0$Se, $\dot{-}_0$Cu, +Zn, +Pb	+L, $\dot{-}$Hg, −Se	−SX, $\dot{+}$L, $\dot{+}$Hg, $\dot{+}$Cu
Cu	+SX, $\dot{-}_0$L, +Se, +Zn	$\dot{+}_0$Se, +Zn	+Se	−Hg, $\dot{+}_0$Cd, +Zn
Zn	$\dot{-}_0$Se, +Cd	+SX, $\dot{-}_0$L, +Cd, +Cu	+Hg, $\dot{+}$Cu	−L, +Se, +Cu
Pb	−L, $\dot{+}_0$Se, $\dot{-}_0$Cd	+Cd	$\dot{+}_0$L	

Furthermore, the Hg levels in marine mammal livers appear to vary greatly from place to place, as a compilation of the available data has shown (Wagemann and Muir 1981). In narwhal kidney and muscle tissue the Hg levels are on the average 1.71 μg/g (wet wt) and 0.85 μg/g (wet wt), respectively, which are comparable with levels in the corresponding tissues of other cetaceans from this area (Wagemann and Muir 1981). The available data for Hg in whale tissues is, however, rather sparse.

The Cd concentration in narwhal kidney and liver tissue is higher than in corresponding tissues of other whales and seals, but the comparison is uncertain in view of the few literature data available (Wagemann and Muir 1981). The source of this Cd is not known. A localized source of metal pollution of the aquatic environment, such as a mining or refining operation, understandably can elevate the metal levels in sedentary organisms in the immediate vicinity of such a facility (Fallis 1982). However, a single point source could only be a substantial source of heavy metals to migratory animals such as whales if these animals spent considerable time in the vicinity of the source.

While oceanic heavy metal concentrations are generally very low, rivers, estuaries, and coastal water bodies can have relatively higher "natural" concentrations, particularly if the adjacent terrain is metalliferous. Surface water concentrations in Strathcona Sound are higher for some metals than would ordinarily be expected for such water. These data (Table 2) represent background levels, as they were taken prior to any mining activity in the area. This sound is an arctic fjord and there is evidence that metal levels are also elevated in another fjord in west Greenland (Bondam and Asmund 1974). Not coincidentally, there are now Pb−Zn mines in both areas and therefore metalliferous deposits are obviously present there. To what extent such levels can be considered typical of arctic coastal waters is largely speculative, since there is a lack of such data from other locations.

Another factor to be considered is the mobilization of metals from carrier particles by chloride ions and chelating substances, which may increase the availability to marine biota with subsequent bioaccumulation (Beijer and Jernelov 1978). Phytoplankton and zooplankton absorb heavy metals and are possibly key factors in the transfer of heavy metals from the water column to higher organisms and sediments. Aquatic plants may take up heavy metals from water directly by a process of passive diffusion (Bryan 1969). It appears that some animals can also absorb them from the water, as distinct from food, by such a mechanism, e.g. the absorption of Zn by puffer fish (Saltman and Burroughs 1960), Cd by shrimp and mussels (Fowler and Benayoun 1974), and Zn and Cd by worms (Bryan and Hummerstone 1973).

We don't know if heavy metals are also absorbed directly from the water into tissues by mammals such as narwhal, but we assume that the primary intake of heavy metals in narwhal is via its food. As we have no data for prey metal concentrations, we can only speculate on ecological pathways. The prey of narwhal are themselves primarily carnivores. Another confounding factor in interpreting such data is the fact that the narwhal is migratory. Although all our samples were obtained from the same locality, the population probably overwinters along the coast of Greenland or in the pack ice of Davis Strait. The overwintering areas for the species are not precisely known, but each spring, narwhals enter the eastern Arctic and migrate to their summering areas. In general, the reverse migration occurs in the fall. The diet of narwhal appears to be primarily nektonic, consisting of squid, Arctic cod (*Boreogadus saida*), shrimp, and Greenland halibut (*Reinhardtius hippoglossoides*) (Mansfield et al. 1975). More recent work (Finley and Gibb 1982) indicates that while in the vicinity of Pond Inlet (where our samples were taken), narwhal feed predominantly upon Arctic cod and Greenland halibut. The latter are presumably taken at considerable depth and appear to be important food items for male narwhals. The same authors report little feeding by narwhals during August; they probably resume feeding in September. After this period, when the narwhals were outside our study area, it is possible that squid were the principal dietary item. It is therefore not known where the narwhals would have been exposed to higher concentrations of Cd in particular, but it would appear reasonable to assume that maximum exposure would occur in coastal areas.

There may be a bimodality with respect to Cd within our relatively small sample (Fig. 1). Future work may elucidate further this trend, and if such a bimodality is real, this may provide evidence of different animal stocks. Such data are necessary for resource management, and should it be possible to correlate differing metal concentrations with differing

stocks, this would provide information on the as yet unknown precise migration history of such stocks. It could provide information on where such animals picked up their metal burdens and perhaps provide an index of stock separation. It must be noted, however, that the Cd concentration varied greatly from animal to animal (i.e. large standard deviation), particularly in kidney tissue (Table 3) and that only a subgroup of the animals examined had relatively high Cd concentrations in the kidney (400–700 μg/g dry wt) (Fig. 1). It is not known whether this might have been due to an efficient uptake by the animals of readily available Cd or due to an inefficient elimination of this metal by the kidney. A quantity that conveys the net result of uptake and elimination is the half-life of the element in the organ or animal. It is known that the half-life of Cd in mammalian kidney varies greatly with species (e.g. 3 yr for mice and 10 yr for man) (Matsubara-Khan 1974; MARC Report No. 20 1980). For narwhal (and for most marine mammals in general) this information is unfortunately not available.

There appear to be no published data available for lead in cetaceans and only a few such data are available for seals (Anas 1974; Holden 1975; Roberts et al. 1976; Drescher 1978). In comparison with the available data, the average concentrations of Pb in kidney and liver of narwhal (0.018 and 0.028 μg/g wet wt, respectively) (Table 3) appear to be lower than in many of the corresponding tissues of seal. Zinc and Cu concentrations in tissues of narwhal are within the range of reference values for other marine mammals (Wagemann and Muir 1981). The average concentration of Se in narwhal liver (4.06 μg/g wet wt) is considerably lower than in the same tissue of other whales and seals, but the comparison is again uncertain in view of the limited number of data in the published literature.

Of the seven elements analysed, only Zn and Cd were consistently higher in kidney than in the liver. This is in accordance with the known distribution pattern of these two metals in mammalian tissues (Bowen 1966; Coombs 1979). In the case of Zn this may be related to the fact that kidney alkaline phosphatase requires Zn as a cofactor (Mathias 1958). In cetaceans, alkaline phosphatase is known to be concentrated also in the kidney (Geraci and St. Aubin 1979). Cadmium is apparently not an essential element for mammals as is Zn, but it is chemically similar to Zn and therefore could possibly mimic Zn in certain biological processes. Cadmium administered intravenously to land mammals is taken up largely by the liver first, but after this initial uptake the concentration in the liver decreases, and that in the kidney increases (Samarawickrama 1979). It is noteworthy in this connection that the partial regression coefficient of Cd concentration on length was negative for liver tissue but positive for kidney tissue (Table 4), which would indicate a decrease with time in the Cd burden in the former tissue but an increase in the latter tissue. This is in accordance with the above-mentioned experimental findings.

Mercury was consistently, positively correlated with length for every tissue except liver, which would appear to indicate that this element is being accumulated with time in these tissues. This interpretation rests on the fact that length is generally a monotonically increasing function of time. A number of workers (Sergeant 1980; Gaskin et al. 1979; Smith and Armstrong 1975; Drescher et al. 1977; Heppleston and French 1973) have already demonstrated that Hg accumulates with age of animal in porpoises and seals. On the other hand, since Cu (in females) and Pb are negatively correlated with length for liver tissue, these metals are apparently being lost with time from this tissue. Alternatively, the concentrations are simply being diluted through the process of growth of these organs and tissues. In this connection it is interesting to note that fetuses of seals (particularly a Leopard seal fetus from the Antarctic) had higher Cu concentrations in their livers than did adult seals (Wagemann and Muir 1981). Such a negative correlation between length of animal and Cu concentration has also been found for Arctic cod by Bohn and McElroy (1976).

A further consideration in the interpretation of heavy metal burdens in animals must be the ameliorating mechanisms such as the synergistic interactions of other elements with the metal and the binding of some heavy metals to the low molecular with protein thionein. The Cd in the kidney and liver of narwhal may be associated with this protein, i.e. Cd–metallothionein, and in this form the metal may be quite innocuous. Largely from work on terrestrial mammals there is increasing evidence that Cd in mammalian renal and hepatic tissues is associated with this low molecular weight protein. Work on the California sea lion (Lee et al. 1977) and the grey seal (Olafson and Thompson 1974) has shown that metallothionein also occurs in the corresponding tissues of marine mammals. The strong association found between Zn and Cd in liver tissue and between Zn and Cd and Cu in kidney tissue (Table 4) may be a reflection of the presence of this substance. We are at present investigating the existence of this protein in tissues of narwhal, with its possible implication in the detoxification of Cd in these animals.

The most interesting interaction between elements appears to be that between Hg and Se. Mercury concentration is strongly correlated positively with Se concentration in narwhal in liver and kidney tissue. Additionally, Se and Hg are associated with a number of other elements. Fairly extensive literature exists on the correlation between Hg and Se in mammalian and fish tissues. Selenium apparently exerts a protective influence against the toxicity of Hg in fish (Ganther et al. 1972) and also appears to govern the accumulation and affect the toxicity of Hg in mammalian tissues (Parizek et al. 1968; Potter and Matrone 1974; Chen et al. 1975; Hansen and Kristensen 1979). The mechanism of this protective influence is not known. It is quite probable, however, that in other animals, also, and not just narwhals, Se correlates with more elements than Hg, but other studies that would show this have apparently not been carried out to date. The atomic concentration ratio Hg/Se is claimed to be most frequently near 1 for liver tissue of marine mammals (Koeman et al. 1975). For narwhals this ratio is on the average (as calculated from the average concentrations of Hg and Se, Table 3) 0.59 for liver tissue, 0.21 for kidney tissue, 0.75 for muscle tissue, and 0.15 for blubber. These ratios obviously depend on the concentration of those other elements with which Hg or Se are correlated (Table 4). A linear relationship between the log-transformed concentrations of Hg and Se was found by Koeman et al. (1973) for liver tissue of different marine mammals. The average concentrations of Hg and Se obtained

by us in narwhal liver fitted their graph quite well. The association between Hg and Se appears to be quite general. Irrespective of the abovementioned potential internal protective mechanisms, it is clear that some metals (e.g. Hg and Cd) increase in concentration with time in certain narwhal tissues and organs. In addition, Cd is present in some animals at much higher concentrations than would be expected in comparison with global concentrations in marine mammals.

Although there is an indication that some metal levels increase with time (and therefore age), the rates, sources, and physiological thresholds are unknown. At this time we are not prepared to postulate any cause and effect relationships between the elements, although further analyses are under way in an effort to elucidate not only interelement patterns but also to quantify intertissue relationships. A better understanding will also depend on a reliable means of ageing. As a next step, age-specific metal concentrations should be determined. Further studies should also elucidate the metal concentrations in organisms from the lower trophic level and the rates and modes of transfer, both in the ecosystem and in the narwhal.

Acknowledgments

We sincerely thank the following persons for their assistance in the preparation of the manuscript: R. Hunt, K. C. Tam, M. Dajic, J. Maniar, R. Blosmanis, E. Marshall, G. Decterow, H. Sequeira, and A. Blouw. We also thank LGL Ltd. and Ms H. Silverman for sample collection and preservation and Drs T. G. Smith and B. Siniff (through the auspices of the National Science Foundation) who provided additional mammal material from the Antarctic. We are especially grateful to Messrs F. A. J. Armstrong and B. Fallis, Dr D. E. Sergeant, Dr J. C. McKie, and P. Johansen for allowing us to refer to hitherto unpublished data and also to Dr R. A. Davis, Mr F. A. J. Armstrong, and Drs W. Franzin and J. Klaverkamp who provided helpful comments on earlier drafts of the manuscript. Finally, we acknowledge the assistance of Mr V. J. Boyko and Dr J. McLaren (National Research Council of Canada) for verification of sample analyses.

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Uptake and Conversion of Selenium by a Marine Bacterium[1]

A. FODA, J. H. VANDERMEULEN,[2] AND J. J. WRENCH

Marine Ecology Laboratory, Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

FODA, A., J. H. VANDERMEULEN, AND J. J. WRENCH. 1983. Uptake and conversion of selenium by a marine bacterium. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 215–220.

Bio-conversion of Se was examined by incubating *Pseudomonas marina* in seawater containing either selenite ($Na_2Se^{IV}O_3$) or selenate ($Na_2Se^{VI}O_4$). At the concentrations of selenite and selenate used (10^{-4}–10^{-7} mol/L), the growth of *P. marina* was not inhibited. Under these conditions, selenite was taken up by *P. marina*, but selenate was not found to enter the cells. *Pseudomonas marina* incorporated selenite from filtered seawater into subcellular fractions, primarily protein (30–50%) and amino acids (44–70%). When incubated in marine broth, *P. marina* incorporated ^{75}selenite primarily into protein (up to 75%), with a lesser amount into the amino acid fraction (approximately 25%). Insignificant amounts were associated with the bacterial lipid fraction. Se^{IV} was found in the protein and amino acid fractions within 10 min of incubation in medium containing selenite. In uptake studies the level of Se^{IV} in the incubating medium decreased markedly, corresponding presumably to Se^{IV} entering the bacterial cells from the medium. However, simultaneous measurements of total Se in the medium (gas–liquid chromatography following photooxidation) revealed an increasing amount of non-Se^{IV} species of Se in the medium throughout the same period. These results were interpreted as due to the bioconversion of selenite by *P. marina* into water-soluble non-Se^{IV} metabolite(s) and their subsequent release back into the medium. Up to 35% of the total Se found in the medium after 24 h can be accounted for by this conversion of Se^{IV} into another oxidation state. *Pseudomonas marina* is also capable of reducing Se^{IV} to elemental Se; this pathway becomes increasingly evident at higher concentrations of Na_2SeO_3.

FODA, A., J. H. VANDERMEULEN, AND J. J. WRENCH. 1983. Uptake and conversion of selenium by a marine bacterium. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 215–220.

Nous avons étudié la bioconversion du sélénium en incubant *Pseudomonas marina* dans de l'eau de mer contenant soit du sélénite ($Na_2Se^{IV}O_3$) ou du séléniate ($Na_2Se^{VI}O_4$). Aux concentrations utilisées (10^{-4} à 10^{-7} mol/L de sélénite et de séléniate), la croissance de *P. marina* n'est pas retardée. Dans ces conditions, le sélénite est absorbé par *P. marina*, alors qu'aucune pénétration de séléniate dans les cellules n'est observée. *Pseudomonas marina* incorpore le sélénite de l'eau de mer filtrée dans des fractions subcellulaires, principalement en protéines (30–50 %) et en acides aminés (40–70 %). Lorsque incubé dans un bouillon marin, *P. marina* incorpore ^{75}sélénite surtout en protéines (jusqu'à 75 %), une quantité moindre en fraction acides aminés (environ 25 %). De minimes quantités sont associées à la fraction bactérienne. On trouve Se^{IV} dans les fractions protéines et acides aminés en moins de 10 min d'incubation dans un milieu contenant du sélénite. On constate, dans des études d'absorption, que le niveau de Se^{IV} dans le milieu de culture diminue notablement, ce qui correspond probablement au Se^{IV} du milieu pénétrant dans les cellules bactériennes. Cependant, des mesures simultanées de Se total dans le milieu (la chromatographie d'un gaz–liquide après photo-oxydation) montrent une quantité croissante de sélénium autre que Se^{IV} dans ce milieu pendant toute cette période. Selon notre interprétation, ceci résulte de la bioconversion du sélénite par *P. marina* en métabolite(s) autre(s) que Se^{IV} soluble(s) dans l'eau et leur mise en liberté subséquente dans le milieu. On peut expliquer par cette conversion de Se^{IV} en un autre état d'oxydation jusqu'à 35 % du Se total observé dans le milieu après 24 h. *Pseudomonas marina* peut également réduire Se^{IV} en Se élémentaire; cette voie devient de plus en plus évidente aux concentrations plus élevées de Na_2SeO_3.

Received April 14, 1982
Accepted December 20, 1982

Reçu le 14 avril 1982
Accepté le 20 décembre 1982

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Author to whom correspondence should be addressed.

Printed in Canada (J6899)
Imprimé au Canada (J6899)

As concern over metal pollution in the offshore marine environment becomes increasingly prominent (e.g. Goldberg 1976), interest is turning to the various mechanisms that govern metal behavior and metabolism in the sea. In this respect, Se serves as a model metal because it is commonly and widely distributed in the marine environment, and both oxidized and reduced forms are found at ultratrace levels (Se^{IV}, 50–800 pmol/kg; Se^{VI}, 500–1500 pmol/kg) (e.g. Sugimura et al. 1976; Measures and Burton 1980a; Measures et al. 1980; Cutter 1982). It is also readily available for uptake by a range of marine organisms such as phytoplankton (Wrench 1978), molluscs (Fowler and Benayoun 1976; Wrench and Campbell 1981), crustaceans (Fowler and Benayoun 1976), fish (Mackay et al. 1975), and marine mammals (Koeman et al. 1973). Physiologically, Se can act as a functional analogue of sulfur. In that role it may follow existing pathways of sulfur metabolism to become incorporated into protein as seleno-analogues of sulfur-amino acids (e.g. Stadtman 1974). It is also a component in certain Se-based enzymes (e.g. Jones et al. 1979).

Oddly enough, despite this pervasive presence of Se in the marine environment, relatively little is known of its behavior or of its bioavailability to and movement through the marine food chain. Yet, a recent study has shown that the levels of one species of Se, Se^{IV} (selenite), are closely linked to biological cycles in the water column and that Se^{IV} can cycle very rapidly through phytoplankton communities (Wrench and Measures 1982). On the other hand, the second major Se species, Se^{VI} (selenate), appears to be biologically unreactive, moving only slowly through the phytoplankton. The reasons for this unequal uptake and cycling of these two Se species are not clear, but one is reminded of dissimilar Se^{IV} and Se^{VI} distribution profiles found for the open ocean where the Se^{IV}:Se^{VI} ratios vary with depth (Measures and Burton 1980a; Measures et al. 1980). In that instance, attention was drawn to a biological involvement in the Se cycle whereby biological discrimination between Se^{IV} and Se^{VI} aids in maintaining this ratio.

Given the surmised close link between Se and the marine biological cycle, and its ready bioavailability and incorporation into basic biological macromolecules in the marine food chain, it became of interest to examine the role of marine bacteria in the bioconversion of Se. Although some data exist for soil microbes (e.g. Doran and Alexander 1977; Brown and Shrift 1980) and freshwater microbes (Silverberg et al. 1976), none are available for marine microflora. Specifically, we examined the toxicity tolerance and the uptake and conversion of selenite and selenate in a marine bacterium *Pseudomonas marina*. We also followed the incorporation of selenite into the intracellular macromolecule pools and the release of Se by the bacterium into the medium.

Materials and Methods

Pseudomonas marina was incubated with either selenite (Na_2SeO_3) or selenate (Na_2SeO_4). Uptake of Se was determined by measuring loss of Se^{IV} or Se^{VI} from the incubating medium, confirmed by parallel determinations on the cells. Intracellular incorporation of Se was followed by incubating cells in radioactive ^{75}Se and extracting the lipid, free amino acid, and protein fractions. The release of Se was determined either visually (Se precipitation), chromatographically (methyl-Se), or by mass balance calculations.

Incubation Conditions

Cultures of *P. marina* (ATCC 25374) were maintained routinely as stock cultures on marine agar (2216, Difco) at 5°C. Twenty-four hours prior to experiments, a single bacterial colony was lifted from the agar and incubated in 10 mL of liquid medium (marine broth 2216, Difco) in the dark at 26°C for 16 h. This temperature is optimum for *P. marina*.

For growth and Se tolerance experiments, 100 mL of filtered marine broth containing desired concentrations of either selenite or selenate was inoculated with 1 mL of the overnight culture and incubated as above (Psychrotherm, 100 rpm). Growth was monitored by optical density readings (500 nm, Pye Unicam SP 1700, UV), with confirmation from total viable plate counts. In experiments with high Se concentrations ($>10^{-4}$ mol/L), total viable plate counts became the method of choice because the formation of elemental Se in the culture flasks interfered with the optical density method.

For the uptake and conversion experiments, bacterial cells were first grown in marine broth as outlined above. Cells were then harvested by centrifugation (10 000 × g) and resuspended in sterile filtered seawater (0.45 μm, Millipore) containing selenite or selenate. We would have preferred to inoculate directly into filtered seawater, but as commonly occurs, such single inocula did not grow. For this reason, cells were begun in marine broth for 16 h, transferred to filtered seawater, and then exposed to Se. Inocula begun in this way maintained their normal viability. At the end of the experiments the cells were again harvested by centrifugation. When analyses were not done immediately, the pellets were washed several times with filtered seawater and stored frozen (−4°C) for no more than 5 d.

Selenium Determinations

Dissolved Se^{IV} (in the medium) was determined after removal of the cells by centrifugation, essentially by the method of Measures and Burton (1980b). After acidification with concentrated HCl (1 mL/100 mL) and removal of interfering organics with toluene (2 × 50 mL), the Se^{IV} was complexed with 1 mL of 4-nitro-*O*-phenylenediamine (NPD) for 1.5 h in the dark. The resulting 5-nitropiaz-selenol complex was then extracted into 1 mL of redistilled toluene. Aliquots were analyzed by electron-capture gas–liquid chromatography (2.44 m × 2 mm glass column, GP 4% SE-30/6% SP-2401 on 100/120 Supelcoport, column temperature 175°C, detector temperature 250°C, gas flow 20 mL/min) (Hewlett-Packard 5700).

Recovery of Se extracts was calculated from recovery of radioactive ^{75}Se tracer carried in parallel through all digestion and extraction procedures. Appropriate blanks were also included in all experiments to provide control and background levels of selenite and selenate.

Recovery of Se from marine broth or from seawater media differs markedly, based on recovery calculations. Thus, we were able to recover only about 13% Se from cell-free marine

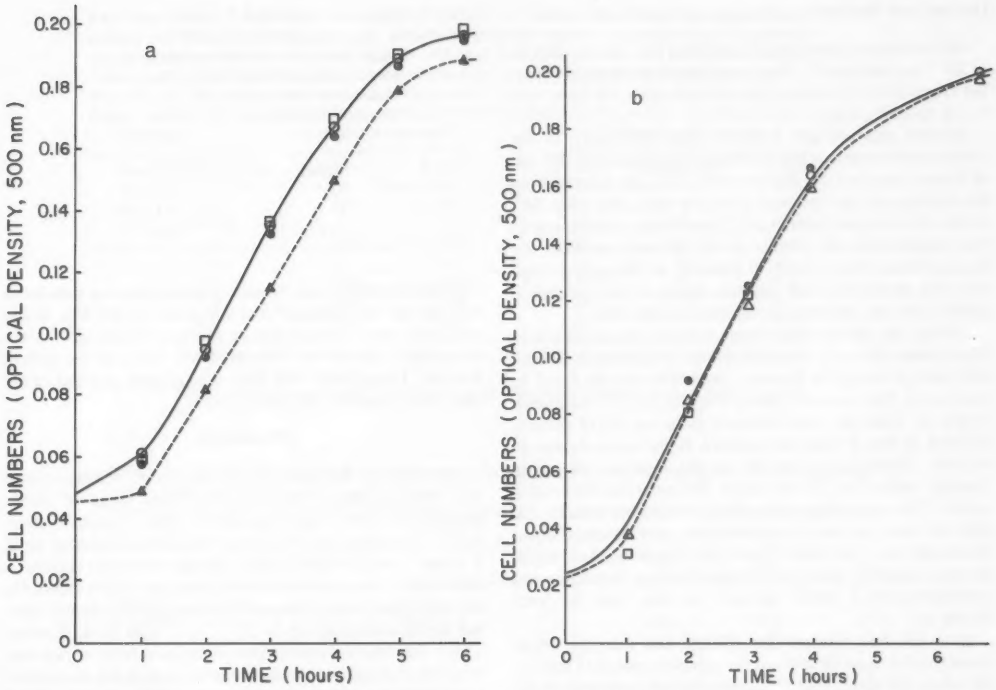

FIG. 1. (a) Growth of *P. marina* in selenite (Na_2SeO_3). ○, control; □, 10^{-5} mol/L; ●, 10^{-4} mol/L; ▲, 10^{-3} mol/L. (b) Growth of *P. marina* in selenate (Na_2SeO_4). ○, control; △, 10^{-7} mol/L; □, 10^{-5} mol/L; ●, 10^{-4} mol/L.

broth media versus 54% from cell-free filtered seawater. For this reason, and for relevance to future water column studies, subsequent uptake experiments were all done using filtered seawater, after initially starting growth in marine broth.

For Se^{VI} and total Se determinations, the photooxidative step described by Measures and Burton (1980b) was used first to convert these species to Se^{IV}. Cell-free medium (100 mL), together with 2 mL of 0.1 mol borate/L and 200 μL of H_2O_2 were UV-irradiated (1000 W) for 5 h and then acidified. From this point on, the procedure was the same as that for dissolved Se^{IV}.

For determination of Se taken up into cells the method followed was that of Cappon and Smith (1978), with the modifications outlined by Wrench and Campbell (1981).

Distribution of Se into the intracellular amino acid and protein pools was followed by incubation with radioactive ^{75}selenite. After incubation, *P. marina* cells were harvested by centrifugation, washed several times with 0.9% NaCl, resuspended in 2 mL of NaCl, and disrupted sonically (Biosonik, 15 mins). Lysed cells were extracted with chloroform–methanol (Folch et al. 1957) and centrifuged to effect phase separation (1500 × g, 10 mins). The upper aqueous phase (CH_3OH-H_2O) containing amino acids was sampled directly for liquid scintillation counting (LC). The pellet, containing insoluble protein, was resuspended in methanol–water (3:2) and counted (15 mL of Atomlight, Beckman LS 3133). The remaining lower chloroform phase, containing the cell lipid fraction, was counted as well for completeness. It was first evaporated under N_2 and then resuspended in methanol–water (3:2) before counting.

Results and Observations

TOLERANCE AND GROWTH

Pseudomonas marina control cultures grew as well as cultures grown in Na_2SeO_3 concentrations of $10^{-7}-10^{-4}$ mol/L (Fig. 1a). At higher concentrations of selenite, growth was somewhat inhibited. In the case of selenate, no reduction in cell growth was noted over the concentration range tested, i.e. $10^{-7}-10^{-4}$ mol/L (Fig. 1b). The 6-h growth curves for both selenite and selenate show no obvious differences from control growth curves, and the various cultures were indistinguishable from control cultures in (a) length of lag phase and onset of log phase, (b) slope of log phase, and (c) level and onset of the plateau. In this respect it is interesting to note that the 6-h growth curve for *P. marina* incubated with 10^{-3} mol selenite/L (Fig. 1), a concentration that limits growth of *P. marina* (Table 1), shows a delayed lag phase with delayed onset of log phase and lower plateau level.

Uptake and Release

All experiments were carried out using 10^{-7} mol selenite/L or 10^{-7} mol selenate/L; these concentrations have no apparent effect on the growth of the cells and are at the lower end of the tolerance range.

Selenite and selenate behaved quite differently in the uptake experiments. When incubated with selenite in 100 mL of filtered seawater, *P. marina* readily took up selenite from the medium and incorporated it into the cells; after 24 h, Se^{IV} in the cells increased from 0 to 1.3 nmol while simultaneously the concentration of selenite in the seawater medium decreased from 10 to 4 nmol. In contrast, no decrease in selenate was observed in the medium during a 24-h incubation period, nor was any selenate detected in the cells.

During the uptake experiment, selenite concentrations in the medium showed a steady decrease, with about 25% selenite removal during the 1st hour, about 40% over the first 5 h, and nearly 70% removal during the first 24 h of incubation (Table 2). Total Se, while showing the same sort of pattern, differed in that it was not removed to the same degree as selenite. Decrease in total Se in the medium was more gradual, with a loss of only about 36% over the entire 24-h period. Thus, at the beginning of the experiment, selenite and total Se were present in equal amounts and remained equal during the first few hours. Over time, however, their levels diverged steadily, with a more rapid decrease in selenite and simultaneously a slower decrease in the total Se level (Table 2).

In a cell-free medium the selenite and total Se levels remained the same throughout the exposure period (Table 3). However, the addition of *P. marina* resulted repeatedly in the observed differential changes in selenite and total Se. In contrast, in media containing selenate only, no change was observed in the selenate levels, either in cell-free preparations or in those containing *P. marina* cells (Table 3).

The possibility of the production and release of methylated Se by *P. marina* was investigated by headspace sampling and analysis by gas-liquid chromatography. The results, while negative, were considered inconclusive, since problems with the sampling method precluded our being absolutely certain that these products were detectable.

On the other hand, Se as free elemental Se could be readily determined visually in cultures of *P. marina* incubated at high concentrations of selenite (i.e. $>10^{-4}$ mol/L). In such cultures a rich red precipitate could be seen microscopically interspersed between the bacterial cells in the medium. No further identification of free Se was carried out.

Intracellular Incorporation

Results differed somewhat depending on the incubating medium used, i.e. whether marine broth or filtered seawater. In the case of the incubations in ^{75}Se-labeled seawater, over 50% of the added label was found in the free amino acid fraction, with the remainder found in the protein fraction (Table 4). The opposite was found when marine broth was used as the incubating medium, with up to 75% of the label associated with the protein fraction and only 25% in the amino acid fraction.

Incorporation occurred quickly. A time-course study of ^{75}Se incorporation from labeled seawater showed that about 82% of the incorporated label was found in the free amino acid pool after only 10 min of exposure (Table 2). At the same time, 16% of the ^{75}Se label was found in the protein fraction. Throughout, only trace to negligible amounts of the label were found in the lipid fraction.

Table 1. Growth of *P. marina* after 24 h at higher concentrations of selenite (marine broth, Difco). Growth was measured by viable plate counts (colony-forming units (cfu)).

Selenite concentration (mol/L)	*P. marina* growth (cfu/mL)
Control	1.7×10^{9}
10^{-3}	2.1×10^{8}
10^{-2}	1.1×10^{7}
2×10^{-2}	0.98×10^{7}

Discussion

The toxicity threshold for *P. marina* to selenite (about 10^{-3} mol/L) agrees well with the broad range of values reported for other microorganisms. Thus, *Chlorella pyrenoidosa* tolerates concentrations of seleno-methionine up to 2×10^{-3} mol/L (Shrift 1960), although *Chlorella vulgaris* is inhibited by somewhat lower concentrations (Shrift 1954). On the other hand, many *Salmonella* species can apparently tolerate media containing up to 2.6×10^{-2} mol Se/L (Leifson 1936), and *Micrococcus selenicus*, isolated from marine harbor mud, is reported to tolerate unusually high but unspecified concentrations of selenite (Brenner 1916, cited in Shrift 1967). No toxicity threshold was established for Se^{VI}; presumably it is $>10^{-4}$ mol/L.

Given these thresholds we were satisfied that the concentrations of selenite and selenate used in our experiments (approximately 10^{-7} mol/L) were well within the tolerance levels of these species and were relevant to concentrations encountered in oceanic waters (e.g. Measures and Burton 1980a). It is possible, however, that these tolerance ranges do not reflect the actual concentrations of selenite or selenate freely available to the cells. As was noted earlier (Materials and Methods section), Se added to either marine broth or to seawater is not completely and equally recoverable. This is especially so in the case of marine broth (containing both trace minerals plus nutrients), where only about 16% of the Se added was subsequently recoverable, presumably because of binding or complexing with some constituent in the broth. Thus, the free dissolved Se available to the cells in these experiments may be an order of magnitude lower in concentration than the total amount accommodated in the medium. This occurred both with cells present and in cell-free preparations. This may also account for some of the variability in Se tolerance reported in various studies and indicates the need for a rigorous analytical approach with adequate assessment of recovery.

Probably the most interesting observations obtained here are those dealing with the metabolism and bioconversion of selenite by *P. marina* and what appears to be the inability of the bacterium to deal with selenate. *Pseudomonas marina*

TABLE 2. Uptake and disposition of selenite in *P. marina* from filtered seawater medium during a 24-h incubation period. Results are from two separate experiments run concurrently under identical conditions. Selenite and total Se in seawater medium was determined by gas–liquid chromatography. Intracellular disposition of selenite into *P. marina* was followed by ^{75}Se incorporation from labeled seawater.

	Se in seawater[a]		^{75}Selenite in *P. marina*[b]		
Sampling time	Selenite	Total Se	Protein	Amino acid	Lipid
Start	100	100	—	—	—
10 min	—	—	16	82	0.2
1 h	74.5	73.9	24	76	0
2 h	—	—	24	77	0
3 h	70.9	69.7	30	70	0.4
5 h	62.3	73.6	24	76	0
24 h	30.6	63.5	30	70	0.4

[a]Data represent percentages of either selenite or total Se detected in 0-h samples (medium with 10^{-7} mol selenite/L).

[b]Data represent percentage distribution of label between the three pools at each sampling time.

TABLE 3. Selenite and total Se levels (percentages) in seawater medium after incubation of *P. marina* with either selenite or selenate (10^{-7} mol/L, 24 h).

Initial Se species	Total Se			Selenite		
	0 h	24 h	*N*	0 h	24 h	*N*
Selenite						
Cell-free medium	100	86.7±5.8	3	100	93.3±15.3	3
With *P. marina*	100	49.3±18.0	3	100	15.3±21.6	3
Selenate						
Cell-free medium	100	100	3	0	0	
With *P. marina*	100	100	3	0	0	

appears to utilize the same route of Se metabolism found in other freshwater and terrestrial bacteria, i.e. the incorporation of selenite into amino acids and cellular proteins (e.g. Doran and Alexander 1977; Stadtman 1974). The results obtained here on uptake and incorporation show that selenite enters very readily into the cells, with rapid incorporation into and equilibration between the amino acid and cellular protein pool. Presumably, this involves formation of seleno-amino acids as described for other such systems (e.g. Stadtman 1974; Doran and Alexander 1977) and parallels the uptake and metabolism of sulfur, its analogue (Gamboa-Lewis 1976; Wrench 1978). This aspect is now under investigation.

We are a little surprised at the apparent inability of *P. marina* to take up selenate from its medium. In this it is clearly different from *Salmonella typhimurium* which readily assimilates both Se species (Brown and Shrift 1980). We had expected that at least some trace amounts of selenate would be detected within the cells, but this was not the case. We can only conclude that selenate, under these experimental conditions, does not enter *P. marina* or that the cells lack selenate reductase and cannot reduce Se^{VI} to Se^{IV}.

The reductive formation of elemental Se by *P. marina* is not too surprising, as this route has been demonstrated in a number of microorganisms (Levine 1925; Doran and Alexander 1977). It is not clear, however, whether the formation of elemental Se is a usual route of selenite metabolism or occurs only at the higher concentrations, near or above the toxicity threshold concentrations. Silverberg et al. (1976), in an electron microscopic study of bacterial Se metabolism, described intracellular Se bodies accumulating in *Escherichia coli* and in a freshwater *Pseudomonas* sp. We did not identify the precise site of elemental Se formation in *P. marina* beyond noting that *P. marina* cultures acquired distinctly red coloring by forming a heavy red precipitate in the bottom of the culture flasks at high concentrations of selenite ($>10^{-3}$ mol/L). Attempts to identify methylated Se released back into the medium proved to be inconclusive. However, in subsequent work now ongoing, one of us has identified the production by *P. marina* of dimethylselenide and dimethyldiselenide as volatile metabolites (J. J. Wrench, unpublished data).

TABLE 4. Percentage distribution of ^{75}selenite into intracellular fractions of *P. marina*, incubated in filtered seawater or in marine broth (Difco) (24 h).

Incubating medium	Protein	Amino acid	Lipid
Marine broth	75	25	0
Seawater	30–50	44–70	0–0.4

One observation made here that may be unique relates to

the observed differences in the medium between the levels of selenite and total dissolved Se following incubation with *P. marina*. That is, the level of total Se in the medium does not decrease at the same rate as does that of selenite, and the presence of *P. marina* significantly alters the percentage composition of the medium in terms of the total Se:Se^{IV} ratio in these 24-h experiments. As this occurs only in incubation with the bacterial cells and not in cell-free preparations, we suggest that this is due to the conversion by *P. marina* of selenite taken up from the medium into a non-Se^{IV} species which is then released back into the medium. The amount of selenite converted by *P. marina* in this manner may be quite substantial. The experiments summarized in Tables 2 and 3 suggest that up to 35% of the total Se present in the medium after 24 h may be a result of this conversion.

At present, we can say very little about the nature of this Se metabolite extruded back into seawater by *P. marina*, beyond the fact that the compound is water soluble, but selenate and seleno-amino acids are the most obvious possibilities. In general terms, the observation of this rapid bioconversion and release of Se emphasizes the relevance of bacterial populations in the marine environment to the biogeochemical cycle of Se.

Acknowledgments

We very much appreciate the critical reading of the manuscript by C. Measures, D. L. Johnson, P. T. S. Wong, and an anonymous reviewer. Their comments served to both clarify the text of this paper and to put our findings in proper perspective.

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Session II — Summary and Overview: Heavy Metals

JOHN W. FARRINGTON

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

AND JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

The past few years have seen substantial progress in marine trace metal studies. Many problems of contamination in sampling and in the precision and accuracy of analyses have been overcome, most notably in the analysis of seawater. A wide variety of papers were presented at this conference within the context of this revolution. However, most results must still be interpreted within a regional or local context. Elevated concentrations of certain trace metals have been identified in certain areas. Unfortunately, despite the progress in sampling and analyses, standardization of basic data still requires more attention via the use of standard reference materials and intercalibration exercises: this is amply demonstrated by Holden et al.

Several papers addressed the role of physical–chemical processes in controlling the movement of trace metals from effluents and other sources into and through estuaries to open ocean areas. Langston compared the behavior of As and Hg in several estuaries in Wales and England. He describes the coprecipitation of As with Fe at low salinities and the correlation of Hg with organic carbon as important in making estuarine sediments accumulation sites for these metals. He also points out the importance of this accumulation to the probable uptake of trace metals by benthic estuarine organisms. The complexity of the relationship between the physical–chemical reactivity and the biological availability of a metal are illustrated by two of Langston's observations. First, As^{3+} has a different estuarine geochemistry than As^{5+} perhaps not unexpectedly. Second, Hg concentrations in tissues of the bivalve *S. plana* and Hg concentrations in sediments seem to be strongly influenced by organic matter content in sediment. There appears to be an inverse correlation between organic matter content in sediments and Hg concentrations in organisms living in the sediments. The reasons for this relationship are unknown but deserving of research. The complex relationships of trace metal distributions between dissolved and particulate phases are reviewed and possible controlling processes are discussed.

Jones and Jeffries report on the substantial surveys of Cd, Cu, Mn, Ni, and Zn in the waters of the shelf waters of the United Kingdom and the open ocean of the North Atlantic. The highest concentrations of the metals occurred generally in coastal waters near major river discharges, suggesting association with freshwater discharges from land as a significant source of input. However, the authors make the important observation that in some cases the source of input is most likely leaching of natural ores and not due to industrial activities. As expected, in some areas of the survey, e.g. Irish Sea, the data were of insufficient density in time and space to clearly distinguish controlling processes. The authors made good use of radionuclide data of others related to a nuclear fuel reprocessing plant to provide a probable explanation of trace metal transport from the extensively industrialized Clyde to some areas of the Irish Sea.

The general conclusions of Jones and Jeffries are that areas of elevated trace metal concentrations are confined to nearshore areas and do not extend very far from shore into areas such as the central North Sea or very far into the Atlantic Ocean. The authors were very careful to point out that this conclusion did not apply to Pb for which they did not obtain data and for which measurements are very difficult. The open ocean data for Cu, Ni, and Zn obtained by these authors adds to the limited number of previous open ocean depth profiles which clearly indicate the coupling of Cu and Ni with biological processes, as reflected by comparison with nutrient depth profiles.

Printed in Canada (J7362)
Imprimé au Canada (J7362)

On the other side of the Atlantic, Yeats and Bewers used box models and mass balance calculations of their data to investigate anthropogenic influences on trace metals in the waters of the Gulf of St. Lawrence. Based on the estimates from these efforts, it appears that riverborne particulate discharges and associated particulate Fe and Mn are almost completely removed from surface waters by the time the water leaves the Gulf at the Cabot Straits. Dissolved Fe is also extensively removed; Ni, Co, Cu, Zn, and Cd are reduced by 20–50% and the dissolved Mn flux is not significantly reduced.

These authors then take a bold step and estimate net efflux rates of these metals from the rivers of the world with accumulation rates in pelagic sediments. This leads them to two important observations. The first has been stated by other workers and is reinforced by the review of current literature: natural processes — mainly biological removal of dissolved metals — impose a natural variability on the large natural metal fluxes to the ocean such that anthropogenic influences on open ocean surface water metal concentrations will only be detected if the anthropogenic influences are large. The second observation is that their comparison of Cd efflux from rivers with Cd accumulation rates in pelagic sediments suggests that the ocean is not in a steady state with respect to Cd. Five times more dissolved Cd and 10 times more particulate Cd appears to be entering than leaving the ocean. This is an intriguing observation deserving further examination as the authors readily admit.

Buckley and Winters respond directly to some of the concerns expressed by other authors about the need for more intensive longer term studies in estuaries to quantify the fluxes of metals to the shelf and open ocean areas. These authors combined seasonal studies over a 2-yr period involving physical oceanography, sedimentology, and geochemistry in the Miramichi Estuary, which feeds into the Gulf of St. Lawrence. A tidal prism model was used to arrive at first-order estimates of fluxes of total suspended particles, particulate metals (Fe, Mn, Zn, Cu, Pb, and Cd), and labile metals. The authors provide important documentation for seasonal influences that should be utmost in the minds of researchers attempting calculations of fluxes to the open ocean via rivers and estuaries. During the spring flood period of an average of 39 d, about 85% of the annual suspended particulate matter load enters the estuary along with 30–55% of the annual supply of labile metals such as Fe, Mn, Zn, and Cu. Much of this flux is remobilized in the estuary over the remainder of the year. This demonstrates the importance of annual cycle studies and the longer term sets of data if we are to have reasonably accurate estimates of the flux of various components from estuaries to the continental shelf areas.

Hunt and Smith used the MERL microcosms to study the release of trace metals from highly contaminated sediments placed in cleaner waters in an experiment simulating conditions following the reduction of pollutant trace metal and organic matter input if pollution abatement were to proceed in an estuary. The particular estuary involved is Narragansett Bay, Rhode Island, but some of the lessons learned are of interest to other estuaries around the North Atlantic Ocean. Measurements and flux calculations showed that Cd, Cu, and Pb were lost from the sediments. The estimate of time necessary to reduce concentrations to natural background concentrations in the upper 1 cm of sediment under the conditions involved were 3 yr for Cd, 44 yr for Cu, and 320 yr for Pb. It is interesting that Fe and Mn were not exported from the microcosms. This differs from the results of Buckley and Winters from the Miramichi Estuary. However, Hunt and Smith carefully consider many constraints on extrapolation of their findings and specifically note that physical dynamics and flushing rates of natural systems can vary depending on the estuary and have a large influence on the rate of loss of metals from sediments. It is important to note that the Miramichi Estuary was studied in its current state in situ without significant changes in inputs or outputs for the past several years. In contrast, Hunt and Smith deliberately manipulated their system to reduce inputs of organic carbon and selected trace metals.

Hunt and Smith also note the unexpected increase in dissolved and particulate Cu in the water column in summer months indicating that Cu can be a very dynamic metal. They also provide an important discussion of the relationship between organic matter loading

in sediments, organic matter oxidation rates, and trace metal geochemistry, especially as these interact in polluted estuarine and harbor sediments, and will be of great importance in understanding trace metal pollution abatement once inputs are reduced or when sediments are dredged and disposed of in other areas of the oceans. Hunt and Smith specifically discuss the important consideration that a reduction in organic carbon loading reduces the organic carbon content of sediment thereby allowing changes in redox conditions which release several metals to the water column (e.g. Cu, Pb, and Cd) and retain some of the Fe and Mn as oxides.

Despite the complexity of the time and space scales of estuarine studies, there have been several efforts to undertake and complete trace metal geochemistry studies. Unfortunately, trace metal geochemical studies in the open ocean area are few and far between. However, as Wallace et al. point out in comparing their study at one station in the Gulf Stream adjacent to the continental shelf of the southeastern United States with other studies, some interesting and consistent patterns are beginning to emerge. The vertical profile of particulate Al in the upper 450 m of the Gulf Stream were consistent with first-order removal processes for the first 100 m and resuspension and/or horizontal transport along isopycnals below 100 m. Downward fluxes of Ni, Cu, Fe, and Mn are consistent with atmospheric fluxes to the surface waters with the possible exception of Mn. Evidently, injection of trace elements from shelf waters into surface Gulf Stream waters are masked by a combination of atmospheric input and large-scale mixing processes.

Thus, we have three papers describing trace metal studies from three separate areas of the open North Atlantic Ocean or assessments of existing data (Yeats and Bewers, Jones and Jeffries, and Wallace et al.) in which the data reflect the recent revolution in trace metal measurements. In each case, and in others in the literature of the past few years cited by these authors, the influence of biological and physical processes on the natural trace metal loading of the oceans apparently accounts for the observed depth profiles and concentrations.

Pb is the obvious and conspicuous exception, but there are still very few open ocean profiles of high-quality Pb measurements. There is little doubt that anthropogenically mobilized Pb is present in the surface waters of the ocean. Unfortunately, no papers at the conference addressed this important issue, most probably because almost all available data has already been published. Those who might have had new data as of September 1981 were contacted but our impression was that few new data points were available.

The biological portions of biogeochemical cycles of trace metals were the subject of a set of papers addressing different parts of the oceanic ecosystems from bacteria to whales.

Foda et al. reported on the role of marine bacteria in the cycling of Se. Both selenite (Se^{IV}) and selenate (Se^{VI}) were added to cultures of two species of bacteria: *Pseudomonas marina* and *Flavobacterium marinotypicum*. Growth of both species was not inhibited. More intensive studies including the use of $^{75}Se^{IV}$ radioisotope with *P. marina* showed that Se^{IV} was preferentially taken up in cells, while Se^{VI} did not appear to enter the cells. Most of the Se^{IV} was associated with proteins and amino acids and insignificant amounts were associated with lipids. During these studies simultaneous measurements of total Se revealed an increase in total Se in the medium, while Se^{IV} decreased, presumably due to uptake by cells. The authors suggest that the bacteria bioconvert selenite to water-soluble non-Se^{IV} metabolites, which are released to the medium. These results join a few recent reports in the literature suggesting similar phenomena in situ. Research over the next several years should unravel many new exciting facets of Se biogeochemistry which are just now being revealed.

Sanders examines biological influences on trace metal cycles by his review of phytoplankton control of the chemical speciation of arsenic in several different culture and microcosm experiments. This control is expressed by the uptake of arsenate via the phosphate transport system and then release as a reduced and a methylated form. Arsenic reduction and methylation appear to be proportional to primary productivity but the form of reduced arsenic present varies spacially and temporally. Sanders hypothesizes that this may be a function of phytoplankton community structure.

The concern with trace metal inputs as real or potential pollutants involves the impact on natural resource populations or on man via food web transfer. Thus, the biological availability, uptake, mobilization, and modification of trace metals is a very important part of biogeochemical cycles with respect to pollution problems. Shears and Fletcher report on regulation of Zn^{2+} in the gastrointestinal tract of winter flounder (*Pseudopleuronectes americana*). Applying mammalian study techniques, they identified similarities with mammalian systems including the competitive effect of Cu^{2+}. However, elevated Zn^{2+} body burdens do not seem to inhibit continued Zn^{2+} uptake across flounder intestines, in contrast with results from mammals. This implies that exposure to elevated Zn^{2+} in the diet of the flounder may not be ameliorated by increasing body burdens with increasing time of exposure. Our knowledge of many aspects of trace metal biochemistry and toxicology in marine organisms is still rudimentary although progress has been made in recent years, as indicated by Shears and Fletcher's own work and discussion of other research.

Wagemann et al. investigated Pb, Cu, Cd, Hg, Se, As, and Zn content of liver, kidney, muscle, and blubber in 60 narwhals (*Monodon monoceras*) from an inlet in the Northwest Territories, Canada. All the elements measured except As were present in lowest concentration in blubber and highest in kidney (Cd, Zn) or liver (Pb, Cu, Hg). Cd had high interanimal variability, which might be expected given the variety of biological factors (see above) capable of influencing Cd in the food web of the narwhal. Hg and Se were highly correlated at the 95% confidence interval, a correlation found by other workers investigating these metals in other components of marine ecosystems. Wageman et al. point out that there is little doubt that narwhals bioaccumulate heavy metals. They emphasize that this fact should be kept in mind when industrial mining activity could lead to releases of metals to their habitat, especially since these whales are harvested by the Canadian Inuit.

The mediation of biological activity of trace metals by organic matter in seawater has been the subject of periodic forays in research over the past several years and is almost always identified as an important topic for trace metal biogeochemical research. Hanson and Quinn provided new significant data on organically complexed Cu and Ni. Their data set is of special interest, since it was obtained in the New York Bight, an area that receives substantial inputs of a variety of pollutants and organic matter from man's activities.

Their data suggest that some dissolved Cu and Ni of riverine and probably anthropogenic origin are transported across the shelf on density surfaces in the water column during the summer, the season of their study. Cu complexed with organic matter is not related in a simple matter to dissolved Cu or other hydrographic features. There is a decrease in organically complexed Cu with increasing distance from the shore towards the edge of the continental shelf.

The isolation of the Cu–organic matter complexes by reverse phase liquid chromatography provided an opportunity to investigate the nature of the organic matter involved in the complexes. The Cu appears to be associated with a variety of labile acidic sites of the dissolved organic matter. Combining these results with theoretical calculations of complexes of Cu in seawater leads to the hypothesis that $CuCO_3^0$ and Cu–humic material complexes are the predominant form of dissolved Cu species in seawater.

Hanson and Quinn report the important observation that the percent of total Cu that is organically complexed is linearly correlated with apparent oxygen utilization. They suggest that this is due to the influence of biological production and consumption of organic matter in shifting the carbonate equilibria and varying the pH of seawater. The latter point, a pH reduction with increased productivity, may be an important factor in Cu complexation confused with the concurrent increase in organic matter exudates by increased productivity. The authors note that field evidence suggests that recently exuded or released dissolved organic matter has no significant effect on Cu complexation.

Most of the organic matter involved in the isolated Cu–organic matter complexes appears to be similar to terrigenous fulvic material. Plots of isolated fulvic acid (reverse phase liquid chromatography) versus salinity suggest that the fulvic acid is being removed by some process as it is mixed across the shelf. Possible removal processes are coagulation

of humic substances, adsorption to particles, photooxidation, microbial degradation, enrichment into sea surface microlayers, or a combination of several mechanisms. It is probable, as the authors point out, that sewage sludge disposal and sewage effluents are a significant source of terrigenous fulvic acid in the New York Bight.

We have discussed Hanson and Quinn's paper last because we think it combines in the data, and more importantly in the discussion, the essence of many of the major findings of the papers at the conference and which are representative of the state of the art in trace metal biogeochemistry. The necessity of investigating the combined influences of physical mixing processes and biological processes on the biogeochemical behavior of total Cu and Cu-organic matter complexes is clearly illustrated. The indirect effect of organic matter production and consumption on pH as a governing factor in Cu–organic matter complexes, not the release of new organic material as exudates, illustrates the importance of a thorough characterization of the system under study and the role of physical–chemical models as interpretive tools in such studies. Finally, the disposal of sewage sludge and sewage effluent release provides an indirect influence on Cu biogeochemistry by introducing terrigenous fulvic acid in addition to being a source of total Cu input.

The papers in this session raise our expectations that there are major new assessments of the influence of biological processes in trace metal biogeochemistry in progress in several laboratories with more exciting discoveries soon to emerge. Other papers have pointed the way towards the required long-term data sets and interactive physical dynamics studies if we are to have good estimates of fluxes of trace metals into and through estuaries to the continental shelf and from the shelf to the central oceans. With respect to open ocean studies, it has been noted by some participants that terms such as "oceanographically consistent data" are being used with increasing frequency in trace metal studies. These participants raised a note of caution that this may lead to the rejection of data and interpretations simply because we do not yet know the nature of the oceanographic processes causing the departure from the expected and known "oceanographic consistency."

Finally, there is a strong realization of the need for a major effort to reliably assess riverine fluxes of trace metals to the oceans. A few excellent studies of a small number of rivers have provided examples of how this can be accomplished.

SESSION III

Ocean Dumping

CHAIRMAN

M. CHAMP

American University, Washington, DC 20016, USA

Projected Consequences of Dumping Sewage Sludge at a Deep Ocean Site near New York Bight[1,2]

THOMAS P. O'CONNOR

Ocean Dumping Program, National Oceanic and Atmospheric Administration, NOAA/N/OMS31, Rockville, MD 20852, USA

AKIRA OKUBO

Marine Sciences Research Center, State University of New York at Stony Brook, Stony Brook, NY 11794, USA

MICHAEL A. CHAMP

The American University, Washington, DC 20016, USA

AND P. KILHO PARK

Ocean Dumping Program, National Oceanic and Atmospheric Administration, NOAA/N/OMS31, Rockville, MD 20852, USA

O'CONNOR, T. P., A. OKUBO, M. A. CHAMP, AND P. K. PARK. 1983. Projected consequences of dumping sewage sludge at a deep ocean site near New York Bight. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 228–241.

Projections are made of the distribution of and biological response to New York/New Jersey sewage sludges if they are slowly discharged from barges at a deepwater location in annual volumes of 7×10^6 m^3. We have used available information on sludge composition, dispersion of barge-dumped wastes, flow through the dumpsite, sewage sludge settling under quiescent conditions, rates of horizontal dispersion in the deep sea, chemical composition of open ocean water, ambient mass fluxes to the seafloor, sediment characteristics, bioturbation rates, and biological responses to sludge and its components. Within a 20-m surface mixed layer between the dumpsite and the Gulf Stream a chemical signal of dumping may be evident in iron, lead, zinc, chromium, and PCB concentrations. Water column contamination would appear to be less than necessary to affect planktonic organisms or fish. Seafloor contamination would be due primarily to sludge particles falling at 10^{-2} cm·s^{-1} or faster. Allowing for bioturbation, the major sediment contaminants, PCBs and PAHs, could reach concentrations at the sediment surface of 0.2 and 0.3 μg·g^{-1}, respectively, after 100 yr. Concentrations of that order in shallow ocean benthic systems are not obviously related to altered benthic life. The strength of these projections would be increased with better understanding in many areas, especially on the effect of natural and barge-induced turbulence on particle flocculation and on rates of horizontal dispersion in the deep ocean. If sludge is dumped, the water column should be studied for chemical evidence of sludge and response of open ocean plankton. Arrays of sediment traps could be deployed to quantify the rate and areal extent of the settling sludge flux.

O'CONNOR, T. P., A. OKUBO, M. A. CHAMP, AND P. K. PARK. 1983. Projected consequences of dumping sewage sludge at a deep ocean site near New York Bight. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 228–241.

Nous présentons ici des projections sur la distribution des boues d'égout de New York/New Jersey et la réaction biologique qu'elles provoquent quand elles sont déversées lentement de barges à un site d'eau profonde, au taux annuel de 7×10^6 m^3. Nous nous sommes servi pour cela des données existantes sur la composition des boues, la dispersion des déchets déversés par les barges, l'écoulement au site de déversement, la sédimentation des boues dans des conditions calmes, les taux de dispersion horizontale dans les profondeurs, la composition chimique de l'eau en haute mer, le flux des masses ambiantes vers le fond, les

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Contribution No. 335 from MSRC/Stony Brook.

Printed in Canada (J6865)
Imprimé au Canada (J6865)

caractéristiques du sédiment, les taux de bioturbation et les réactions biologiques aux boues et à leurs constituants. Dans une couche mixte superficielle de 20 m, entre le site de déversement et le Gulf Stream, on peut observer les effets des déversements par les concentrations de fer, plomb, zinc, chrome et BPC. La contamination de la colonne d'eau semble être moindre que celle qui pourrait affecter les organismes planctoniques ou les poissons. La contamination du fond de la mer résulterait surtout de la chute des particules de déchet à des vitesses de 10^{-2} cm·s^{-1} ou plus. Compte tenu de la bioturbation, les principaux contaminants du sédiment, PBC et PAH, pourraient atteindre des concentrations de 0,2 et 0,3 μg·g^{-1} respectivement après 100 an. Il est évident que des concentrations de cet ordre de grandeur dans les systèmes océaniques benthiques peu profonds n'affectent pas la vie sur le fond. Ces projections seraient plus fermes avec une meilleure compréhension de bien des domaines, surtout l'effet d'une turbulence naturelle ou provoquée par les barges sur la floculation des particules et sur les taux de dispersion horizontale dans les profondeurs océaniques. Si les boues étaient ainsi déversées, on devrait étudier la colonne d'eau et déterminer leurs effets chimiques, et la réaction du plancton de haute mer. On pourrait installer des batteries de trappes à sédiments afin de quantifier les taux et la superficie de sédimentation des boues.

Received March 19, 1982
Accepted November 17, 1982

Reçu le 19 mars 1982
Accepté le 17 novembre 1982

SINCE 1924, sewage treatment plant sludges from municipalities in the states of New York and New Jersey near and including New York City have been dumped from barges at a location 22 km seaward of the Hudson River mouth. In 1972, the United States enacted the Marine Protection Research and Sanctuaries Act which required regulation of ocean dumping of all wastes. A subsequent amendment to that Act has been interpreted to mean that sludge could not be dumped at the presently used site beyond 1981. It is not our intention to enter the surrounding controversy or to recommend a disposal strategy for sewage sludge. We will discuss the consequences of implementing one possible alternative to the present practice: use of a deepwater site dumpsite.

106-Mile Site, Physical Environment

The 106-Mile Chemical Waste Disposal Site has been used since 1973 for the regulated disposal of wastes. The closest deepwater location to New York, it is, as its name implies, 106 nautical miles (191 km) southeast of Ambrose light tower at the entrance to New York Harbor. It is a 1500-km^2 area bounded by 72°00′ to 72°30′W and 38°40′ to 39°00′N (Fig. 1). Water depths average about 2200 m, varying from 1750 m in the northwest corner over the continental slope to 2600 m in the southwest corner over the upper continental rise (Bisagni 1977).

Water column characteristics for the 106-mile site are representative of the slope water regime of the northwest Atlantic, between the edge of the continental shelf and the Gulf Stream. There is a permanent pycnocline at about 100 m and a seasonal pycnocline at about 20 m during May through September (Ingham et al. 1977). Long-term current meter records from Woods Hole Oceanographic Institution's Site-D (39°20′N, 70°00′W) about 190 km northeast of the 106-mile site have been analyzed by Webster (1969) and summarized by Ingham et al. (1977) to indicate an average slope water flow to the west along the contour of the continental shelf. Flow along that same contour at the 106-mile site would be toward the southwest. Satellite-tracked buoys drogued at 10 m have been shown to migrate through the 106-mile site in a southwestward direction (Bisagni 1981). Two buoys deployed at the 106-mile site in September 1980 and three which entered the slope water flow in January 1979 after having earlier been deployed over Georges Bank all moved in conformance to the contour of the continental shelf. They migrated southwest from the 106-mile site at 10−20 cm·s^{-1} and became entrained within the Gulf Stream off Cape Hatteras within about 30 d of passing through the dumpsite. These data reinforce the contention of Ingham et al. (1977) that the Site-D current meter data also describe average flow at the 106-mile site with the exception that flow is directed toward the southwest.

Except for relatively fast-sinking particles, wastes dumped at the 106-mile site are constrained to the upper mixed layer. The flux of water in that layer occurs over a cross-section 20 m deep, in summer, and, conservatively, 60 km wide, which is the distance across the dumpsite perpendicular to the average flow direction. With an average surface current velocity of 11 cm·s^{-1} (Ingham et al. 1977) the flux of water available for dilution of dumped wastes is 1×10^{10} m^3·d^{-1}.

The major deviation from this average riverlike flow occurs with the passage of warm-core Gulf Stream eddies through the slope water regime (Bisagni 1976). If they do not recombine with the Gulf Stream before nearing the continental shelf, these eddies migrate along a path which parallels the shelf contour and eventually are reabsorbed into the Gulf Stream north of Cape Hatteras. When the 106-mile site is within an eddy, it remains so for about 3 wk (Bisagni 1976). The volume of water available in the upper 20 m of a 100-km-diameter eddy is about 2×10^{11} m^3. This corresponds to a volume per day of about 1×10^{10} m^3, the same as that flowing through the dumpsite in the absence of eddies. The overall effect of eddies, therefore, is to alter the short-term flow structure at the dumpsite but not to significantly change its long-term dispersive characteristics.

In this paper, we will use the flux of 1×10^{10} m^3·d^{-1} as the rate of renewal of water above the seasonal pycnocline at the 106-mile site. Once water has passed through the site it

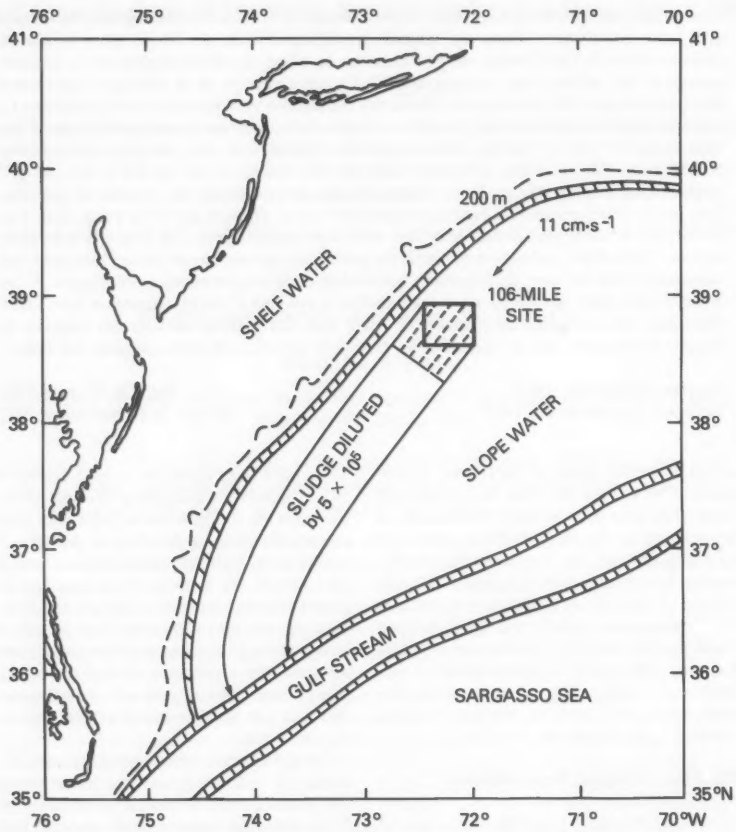

FIG. 1. Location of 106-mile site and nominal locations of fronts separating water masses in the region. Stipled area within and near the dumpsite would contain discrete and growing plumes; to the southwest, sludge would generally be diluted by a factor of 5×10^5 (see text).

will be assumed to be subsequently entrained into the Gulf Stream. Theoretically, the southwest flow along the contour of the continental shelf could be part of the western leg of a slope water gyre (Sverdrup et al. 1942; Csanady 1979). The existence of this gyre, if demonstrated, would imply that some fraction of the water flowing through the dumpsite had previously been there about 1 yr earlier (Csanady et al. 1979). While it does not disprove a gyre's existence, none of the satellite-tracked buoys discussed by Bisagni (1981) returned to the slope water region after being entrained within the Gulf Stream.

Restricting flow from the dumpsite to the Gulf Stream over a 60-km-wide path precludes advection eastward into slope water or westward over the continental shelf. The front (Fig. 1) between shelf water and slope water is not static. On the basis of satellite imagery of sea surface temperature, Ingham (1981) has estimated that for 32% of the time between October 1979 and September 1980 part of the 106-mile site was occupied by shelf water. Such shelf water does not necessarily return westward to the continental shelf. A major mechanism, seen in satellite imagery, for shelf water migration is its entrainment around anticyclonic warm-core Gulf Stream eddies. Such water appears to be mixed, eventually, into slope water (Fischer 1980). Csanady (1983) has pointed out that the general seaward salinity gradient implies a net eastward movement of cold, fresh shelf water to the warm, salty Sargasso Sea. Therefore, while the details of flow in the area of the 106-mile site are complex, our assumption of a 60-km-wide path leading to the Gulf Stream is a reasonable, conservative estimate.

Waste Dispersion, Water Column

As detailed by O'Connor and Park (1982), industrial wastes (8×10^5 m^3 dumped at 106-mile site in 1980) are delivered in lots of 4×10^3 m^3 (1×10^6 gal) and dumped over about

TABLE 1. New York/New Jersey sewage sludge characteristics.

Component	Concentration ($\mu g \cdot g^{-1}$)[a] wet	dry[b]
Total solids	45 000	
Suspended solids	39 000	
Biological oxygen demand	17 000	
Chemical oxygen demand	93 000	
Total organic carbon	9 200	180 000
Total nitrogen	1 500	
Total phosphorus	400	
Cadmium	3.7	74
Mercury	0.5	10
Copper	60	1 200
Lead	63	1 260
Zinc	160	3 200
Iron	1 100	22 000
Chromium	63	1 260
Nickel	9.5	190
Vanadium	0.8	16
Arsenic	0.1	2
Selenium	0.1	2
Total PCBs	0.4	8
Total PAHs	0.7	14

[a]All data except iron, PCBs, and PAHs are from Mueller et al. (1976). Their data represent weighted averages of sludges from individual municipalities in 1973. A perusal of 1980 sludge analysis reports has caused us to decrease the Mueller et al. (1976) value by a factor of 2 and the selenium value (originally misquoted) by a factor of 1000. Furr et al. (1976) include a concentration for iron in New York City sludge. MacLeod et al. (1981) analyzed New York/New Jersey sludge composites for organic compounds. The PAH concentration given here applies to three-ring or larger compounds. Sludge also contains 0.3 μg naphthalenes $\cdot g^{-1}$ and 0.2 μg biphenyls $\cdot g^{-1}$.

[b]On the basis of sludge being about 5% solids, the dry weight concentrations are 20 times the wet weight concentrations.

50-km-long tracks. Wastes are initially diluted under the influence of barge-generated turbulence into 2×10^7-m^3 volumes which are about 10 m deep, 40 m wide, and 50 km long. Thus, initial waste fields are long, narrow strips in which waste has been diluted by a factor of 5000. This extensive initial dilution is sufficient to nullify density differences which exist between seawater and undiluted industrial wastes, whose densities vary from 1.02 to 1.16 $g \cdot cm^{-3}$. Subsequent dilution of waste is due to passive oceanic mixing.

Under relatively calm sea conditions the growth of industrial waste plumes has been observed to be a slow process. Waste distributions deepen to fill the mixed layer which is only about 20 m during summer. Plumes cannot become significantly longer; until horizontal shear breaks them into pieces, there is no concentration gradient in that direction. They widen, on average, at a rate consistent with a diffusion velocity of 1 $cm \cdot s^{-1}$. So after 24 h the initial plume has grown to being 20 m deep, 1 km wide, and slightly longer than 50 km. Within this volume of 1×10^9 m^3 the waste is diluted by a factor of about 2×10^5. If plume growth were to remain steady at 1 $cm \cdot s^{-1}$, a 10-d period would be required to dilute waste by another order of magnitude. Csanady (1981) has discussed the importance of episodic atmospheric or oceanographic events in causing waste plumes to quickly decompose and disperse into the available diluting volume.

If it is assumed that sewage sludge, like industrial waste, is constrained primarily to the upper mixed layer, the average behavior of single sludge plumes will be as just described. However, the projected annual volume of sludge is an order of magnitude greater than that for industrial wastes. In 1980, New York/New Jersey municipalities discarded 7.31×10^6 t of sludge at sea (USEPA 1981). This represents a volume of about 7×10^6 m^3. On a daily basis, 1.9×10^4 m^3 of sludge could have been dumped at the 106-mile site in 1980. The maximum dilution it could have received is the ratio of water flux (1×10^{10} $m^3 \cdot d^{-1}$) to sludge flux, or 5×10^5, about twice the dilution achieved in 1 d due to slow passive oceanic mixing. Therefore, over a 2-d period, sludge would have been diluted to its maximum extent. Beyond that period it would simply have been mixing into water which already contained sludge. When contaminated water is entrained into the Gulf Stream, about 30 d after receiving waste, it is subsequently further diluted, since water transport in the upper 20 m of the stream is at least an order of magnitude greater than the flux through the 106-mile site (von Arx 1962). Figure 1 includes a sketch of the sludge distribution created by a daily disposal of 1.9×10^4 m^3.

Applying the dilution factor of 5×10^5 to the average composition of New York/New Jersey sewage sludges (Table 1) yields an estimate of chemical concentrations (Table 2) within that distribution. Except within fresh and growing sludge plumes, these are the concentrations which would apply if all sludge remained in the upper 20 m. Chemically, the best indicators of the presence of sludge would be those substances whose concentrations increase by a factor of 2 or more (see last column in Table 2). Five sludge components fit this criterion: iron, lead, zinc, chromium, and PCBs. It should be noted that the increased concentrations, even for these substances, are still low. To identify sludge, it would be necessary to exercise the same precautions used in studying "clean" seawater (Bruland et al. 1979).

Economically, if New York/New Jersey sludge is dumped at the 106-mile site, it may be beneficial to somewhat decrease its present 95% water content. Decreasing the water content to 80% would decrease sludge volume by a factor of four. Assuming individual barge loads of 4×10^3 m^3, the daily discharge volume cited above could be accommodated in one instead of four barges. The input of sludge components, except water, would remain constant but their initial concentrations would increase by a factor of 4 and the ultimate dilution factor would increase to 2×10^6. This would mean, again assuming sludge to remain in the mixed layer, that initial plumes would be more concentrated, and up to 10 d would be required for sludge to be mixed into the available diluting volume.

Sludge Settling

Concentrations of sludge in the mixed layer decrease as sludge settles into the deep ocean. Concern for environmental consequences turns from the mixed layer to the benthos. Existing documentation on biological responses to sludge in the ocean emphasizes effects on benthic organisms (e.g. Bascom et al. 1981; Stanford et al. 1981). Jackson et al. (1979) have considered the settling of sludge as determined by

TABLE 2. Comparisons of sludge component concentrations with ambient surface water concentrations. Sludge was diluted by a factor of 5×10^5 (see text).

Sludge component	Concentration ($ng \cdot kg^{-1}$) after dilution (A)	Ambient concentration[a] ($ng \cdot kg^{-1}$) (B)	(A + B)/B
Suspended solids	7.8×10^4	$(10-30) \times 10^4$	1.8–1.3
Oxygen demand (O_2 loss)	1.9×10^5	$(43-70) \times 10^5$ (O_2)	1.04–1.03
Total organic carbon	1.8×10^4	100×10^4	1.02
Total nitrogen	1200	9700 (summer)	1.1
Total phosphorus	800	31 000 (summer)	1.02
Iron	2200	500	5.4
Cadmium	7.4	14	1.5
Mercury	1.0	5	1.2
Copper	120	170	1.7
Lead	126	5	26
Zinc	320	10	33
Chromium	126	70	2.8
Nickel	19	200	1.1
Vanadium	1.6	1500	1.001
Arsenic	0.2	90	1.002
Selenium	0.2	40	1.005
Total PCBs	0.8	0.5	2.3
Total PAHs	0.7	—	—

[a]Data for ambient surface water concentrations of suspended solids, iron, cadmium, and copper are from Kester et al. (1981a). Dissolved oxygen data are from Warsh (1975). Nitrogen and phosphorus concentrations are averages from Peterson (1975). All the above concentrations were measured in slope water in the context of 106-mile site investigations. The remaining concentrations are for open ocean surface waters: mercury (Mukherji and Kester 1980), lead (Settle and Patterson 1980), zinc and nickel (Bruland et al. 1979), chromium (Cranston and Murray 1978), arsenic (Andreae 1979), selenium (Measures et al. 1980), and vanadium (Brewer 1975). The PCB concentration is a low value from Harvey and Steinhauer (1976a) obtained in the vicinity of the 106-mile site. A low value is used because of the mass balance arguments by de Lappe et al. (1980) that ocean concentrations of PCB cannot be of the order of 1 $ng \cdot kg^{-1}$.

gravity and turbulent mixing over an unstratified 50-m-deep water column. For a stratified 2000-m water column we can ignore passive mixing of sludge to the seafloor as a trivially slow process. We consider only gravitational descent of sludge particles themselves or fecal material containing sludge.

Settling velocity distributions have not been measured for New York/New Jersey sewage sludges. Faisst (1981) has made such determinations for southern California sludges. The results, which apply only for quiescent settling conditions, varied somewhat among sludges. Most importantly, the distributions shifted toward faster rates as sludge concentrations increased (Table 3). This was a manifestation of particle flocculation which increased with the frequency of particle–particle collisions yielding larger and faster settling particles. It will be assumed that for New York/New Jersey sludges, 20% of the solids will settle at 10^{-2} $cm \cdot s^{-1}$ or faster and reach the seafloor within the slope water regime. The fraction falling at 10^{-3} $cm \cdot s^{-1}$ or slower will mix only slowly into the deep sea.

A number of considerations are necessary in applying the data of Table 3 to New York/New Jersey sludges. The sludges studied by Faisst (1981) contained about 2.5% solids. The New York/New Jersey sludges are 5% solids. This would tend to increase settling rates. Conversely, slow discharging of sludge from barges can yield initial dilution factors of 5000 which are 10 times more dilute than Faisst's (1981) most dilute suspension. This would decrease the percentage of solids falling at 10^{-2} $cm \cdot s^{-1}$ or faster. The data of Faisst (1981) for three dilutions of Los Angeles County sludge are for a primary sludge. Another sludge containing a mixture of primary and secondary treatment sludges at a 100-fold dilution showed only 10% falling at 10^{-2} $cm \cdot s^{-1}$ or faster. The fact that New York/New Jersey sludges are mixtures of primary and secondary sludges would argue for less than 20% of it falling at the faster rates.

No account has yet been made of the effect of turbulence on sewage sludge settling. Hunt (1982) has discussed the importance of turbulence in detail and has shown its importance in the rate of change of particle sizes of clay suspensions. Turbulence will affect settling velocities in three ways: first, it will increase the frequency of particle–particle collisions, thus increasing flocculation; second, above some critical value of shear, flocs will be destroyed rather than created; third, simply by being the basic mechanism of mixing, turbulence will decrease particle concentrations and thus decrease their frequency of collision. No quantitative application of these effects can be made for New York/New Jersey sludges. Qualitatively, however, if the objective of ocean disposal is to disperse sludge as much as possible, it is important to achieve as much initial dilution as practicable. This will not only reduce the time necessary for sludge to be diluted into the available ocean volume but decrease the rate of flocculation and therefore descent of sludge to the seafloor.

TABLE 3. Distribution of sludge settling velocities (estimated from corresponding figure in Faisst 1981).

Fall velocity ($cm \cdot s^{-1}$)	Dilution[a] 1:50	1:100	1:500	Time to descend 2000 m
10^{-1}	90	95	95	20 d
10^{-2}	70	75	85	200 d
10^{-3}	40	45	70	6 yr
10^{-4}	20	20	30	60 yr

[a]Percentages of total solids falling at less than listed velocities for various sludge dilutions.

With an estimate that 20% of sludge solids will reach the seafloor in 200 d, the settling sludge flux is that mass of particles per unit time spread over the area of horizontal dispersion achieved in 200 d. There are very few data on which to base rates of horizontal mixing below the oceanic mixed layer. Ewart and Bendiner (1981) have reported on dye dispersion at depths of 300 and 1000 m in the Pacific. The diffusion velocity they observed has led us to consider horizontal mixing at those depths to occur 10 times more slowly than in the upper mixed layer. The data of Okubo (1971), which are sparse at times on the order of 200 d, indicate a horizontal area of the order of 10^6 km^2 for mixed layer dispersion over that time scale. Discounting that area for 10 times slower dispersion implies that sludge falling at 10^{-2} $cm \cdot s^{-1}$ would cover a seafloor area of the order of 10^4 km^2.

By the same reasoning, very fast settling (10^{-1} $cm \cdot s^{-1}$) particles would cover only 1 km^2 of seafloor. However, given many separate dumping events over a year's time, sludge could easily be distributed over at least an area equal to that of the dumpsite, or about 1500 km^2. Letting 5% of sludge solids fall onto that area would increase our subsequent estimates of sludge flux and sediment contaminations by a factor of 1.5 for 1500 km^2 of the sludge-affected zone.

In 1980, 20% of the sludge solid input was 7×10^{10} g. Spread over a 10^4-km^2 area, this becomes a flux of 7×10^{-4} $g \cdot cm^{-2} \cdot yr^{-1}$. Rowe and Gardner (1979) measured mass fluxes into sediment traps deployed 30–100 m above the seafloor below the 106-mile site and seaward. Their results, after conversion of units, indicate an ambient mass flux of 4×10^{-3} to 13×10^{-3} $g \cdot cm^{-2} \cdot yr^{-1}$. Thus, the sludge flux would be about 10% of the ambient mass flux.

Pelletization of Sludge

We have allowed particles sinking at 10^{-2} $cm \cdot s^{-1}$ or faster to form the significant flux of sludge depositing on the seafloor. If sludge is incorporated into fast-sinking (hundreds of metres per day) fecal material in the mixed layer, a sludge flux could be estimated from fecal pellet production rates.

The rate of fecal pellet production should be related to the size of the zooplankton population. Sampling in slope water, Sherman et al. (1977) found a zooplankton biomass of 10^{-3}–10^{-1} $g \cdot m^{-3}$ on a dry weight basis, varying with season and among samples during seasons. A median value for all periods was about 10^{-2} $g \cdot m^{-3}$. Elder and Fowler (1977) report a fecal matter production rate for a euphausiid of 2–5% of dry body weight per day. Using a value of 5% dry weight per day and a biomass of 10^{-2} $g \cdot m^{-3}$, the fecal material production rate in the area of interest becomes 5×10^{-4} $g \cdot m^{-3} \cdot d^{-1}$. Over the upper 20 m this converts to 3.7×10^{-4} $g \cdot cm^{-2} \cdot yr^{-1}$. With sludge constrained to that depth interval, the suspended solids concentration would increase by about 50% (Table 2). If zooplankton indiscriminately ingested and pelletized sludge, the sludge flux could be one-half of the total biologically generated flux or about 2×10^{-4} $g \cdot cm^{-2} \cdot yr^{-1}$. This is about one-quarter of the flux due to the faster settling particles. Given that it is less and would decrease further as the sludge contribution to total suspended solids decreases, the flux of sludge as fecal material has not been included in calculating the benthic distribution of sludge.

Bioturbation

On the basis of photographic evidence, Bisagni (1977) and Heezen (1977) described the seafloor of the continental slope and upper rise as depositional. Directly below the 106-mile site, Rowe and Gardner (1979) visually observed bottom water to be free of a nepheloid layer. It is possible that during the period of descent some sludge particles would migrate into the Western Boundary Undercurrent which overlies an erosional regime at depths exceeding 3800 m on the lower continental rise (Heezen 1975). We will assume, however, that once sludge particles have reached the seafloor they are no longer subject to horizontal dispersion.

Dayal et al. (1979) investigated the distribution of ^{137}Cs in sediment near a canister of radioactive waste lying at a depth of 2800 m about 20 km southeast of the 106-mile site. (This 2800-m dumpsite was used for disposal of low-level radioactive waste between 1945 and 1965.) The vertical profile of ^{137}Cs was consistent with a biological sediment mixing coefficient (bioturbation) of 1.1 $cm^2 \cdot yr^{-1}$. As Dayal et al. (1979) explain, this coefficient is high relative to others derived for deep-sea sediments on the basis of distributions of fallout or natural radionuclides. On the other hand, a value of 0.1 $cm^2 \cdot yr^{-1}$ if used to describe the mixing of deposited sludge into sediment will be at the low end of reported coefficients.

The appropriate expression for the distribution of a substance continuously supplied to and diffusing into a plane is (Carslaw and Jaeger 1959)

$$(1)\quad C(x,t) = Q\left[\left(\frac{t}{\pi D}\right)^{1/2} e^{-x^2/4Dt} - \frac{x}{2D}\, erfc\, \frac{x}{\sqrt{4Dt}}\right]$$

where C = concentration of contaminant in sediment (micrograms per cubic centimetre), Q = deposition rate of contaminant (micrograms per square centimetre per year), t = time (years), D = bioturbation "diffusion" coefficient (square centimetres per year), x = depth into sediment (centimetres), positive downwards $C(x,0) = 0$.

The maximum concentration will always be at the sediment surface, thus

$$(2)\quad C_{max}(t) = C(0,t) = Q\left(\frac{t}{\pi D}\right)^{1/2}.$$

The ratio of the concentration at any depth, x, to the maximum concentration is

$$(3)\quad \frac{C(x,t)}{C(0,t)} = \sqrt{\pi}\ ierfc\ \frac{x}{\sqrt{4Dt}}.$$

Equations 1 through 3 apply for a constant D, an x which is independent of time, and yield concentrations of contaminant per unit volume of sediment. Our choice of a constant and low D will tend to minimize the effect of bioturbation. Jumars (1978) has suggested that mixing will be more intense in a very thin surface layer than within sediment below. Conversion of concentration to units of contaminant per unit weight of sediment solids has implications on the validity of holding x constant.

We will assume a sediment which over the depth of interest is 80% water by volume (porosity). Schink et al. (1975) indicated porosity to be approximately independent of depth for deep-sea cores and to range from 64 to 84% over 24 cores. Nozaki et al. (1977) reported sediment bulk densities of about 1.3 $g \cdot cm^{-3}$ for sediments in a core from the mid-Atlantic Ridge (presumably the densities they list are the inverses of measured densities, since density cannot be less than 1). With a solid-phase density of 2.7 $g \cdot cm^{-3}$, which was used by Schink et al. (1975) and is appropriate for sediments which are 50% calcium carbonate such as those below the 106-mile site (Rowe and Clifford 1978), a bulk sediment density of 1.3 corresponds to a porosity of 82%. A median value from Rowe and Gardner (1979) for solids addition to the seafloor in the area of interest is 8×10^{-3} $g \cdot cm^{-2} \cdot yr^{-1}$. If sediment is 80% water by volume the rate of sediment buildup, using a solid density of 2.7 $g \cdot cm^{-3}$, is 0.014 $cm \cdot yr^{-1}$. This is 5 times the rate derived for sediments over the mid-Atlantic Ridge (Nozaki et al. 1977).

The depth of contaminant penetration can be estimated from eq. 3 as the depth where concentrations are 1% of their maxima at the sediment surface. With a constant D of 0.1 $cm^2 \cdot yr^{-1}$ this depth is 1.1, 3.5, and 11 cm after 1, 10, and 100 yr, respectively. Therefore, after 1 yr, the increase in sediment thickness is 1% of the penetration depth and it becomes 10% of that depth after 100 yr. Given that a low bioturbation coefficient is being used and no account for faster mixing near the seawater interface is made, it is reasonable to use eq. 2 to estimate maximum sediment concentrations. On the time scale of 100 yr, it begins to lose validity because of sediment buildup and because the penetration depth is near the maximum to which biological mixing is active (Dayal et al. 1979 and references therein). It is not likely that if sludge is dumped at the 106-mile site the practice will continue for more than 100 yr. Few technical enterprises continue for a century without major modifications.

Sediment Contamination

With the assumptions that sediment is 80% water by volume and the solid's density is 2.7 $g \cdot cm^{-3}$. the maximum concentrations of sludge-derived contaminants are calculated by

$$(4)\quad C_{max}(t) = 1.9Q\left(\frac{t}{\pi D}\right)^{1/2}$$

where C is in units of micrograms of contaminant per gram of dry sediment. The contaminant flux, Q, is defined as the dry weight concentration of contaminant in sludge (micrograms per gram) (Table 2) times the sludge flux of 7×10^{-4} $g \cdot cm^{-2} \cdot yr^{-1}$.

Calculated maximum concentrations for some contaminants (Table 4) can be compared with ambient concentrations and concentrations derived by the following equation where bioturbation is ignored:

$$(5)\quad C' = Q/F$$

where F is the total mass flux (i.e. sludge flux plus ambient). With eq. 5 it is assumed that sludge and ambient particles simply pile up on the seafloor. A concentration so calculated is independent of time or depth in sediment. Comparisons between C_{max} and C' demonstrate the importance of considering bioturbation. After 100 yr, C_{max}, which applies only at the seawater–sediment interface, is 30% of C', which applies throughout the depth of 100-yr sedimentation.

Sludge cannot be biologically mixed into sediment if its presence were to eliminate all but bacterial life through creation of anoxia at the sediment surface. Assuming no oxidation while descending, the sludge flux of organic carbon would be about 1.3×10^{-4} $g \cdot cm^{-2} \cdot yr^{-1}$ or 20% of the ambient organic carbon flux reported by Rowe and Gardner (1979). There is no evidence that bottom oxygen concentrations are close to zero now in open areas of the deep ocean or that a 20% increase in oxidizable material could not be accommodated.

Comparisons with Existing Data

Neither sewage sludge nor any other waste has been dumped at deep ocean sites in volumes approaching 7×10^6 $m^3 \cdot yr^{-1}$. No measurements of the flux of settling waste through the deep ocean have been justified.

Data from studies of sludge dumping over continental shelves into stratified water columns (Callaway et al. 1976; Hatcher et al. 1981) have been examined for evidence that sludge would quickly penetrate a pycnocline. It is important in this context to consider discharge rates. Their importance lies not so much in establishing initial dilutions but in the fact that the rate of particle flocculation and therefore settling will vary inversely with the dilution. Sludge dumped from a stationary barge receives the least initial dilution, yet the figures in Hatcher et al. (1981) show sludge components, i.e. suspended solids, nutrients, and trace elements, only in the mixed layer with the exception of three deeper water analyses of manganese or iron. With sludge dumped at a finite but undefined rate, Hatcher et al. (1981) found no evidence of sludge by conventional analyses anywhere in the water column but did observe a similar concentration of coprostanol (a steroid unique to mammals) both above and below the pycnocline. Callaway et al. (1976) observed dispersion on the basis of transmissometry for sludges dumped at 1600–3100 $m^3 \cdot km^{-1}$. There was some hint of pycnocline penetration but sludge was distributed primarily in the mixed layer.

Chemical analyses for waste dispersion have, until recently (NAE 1981), been limited to discrete samples at isolated

TABLE 4. Sediment contamination due to sludge calculated with (eq. 4) and without (eq. 5) consideration of bioturbation and ambient concentrations (all concentrations in units of micrograms per gram dry wt).

Sludge component	Maximum added concentration in sediment (eq. 4) after: 1 yr	10 yr	100 yr	Added concentration (eq. 5)	Ambient concentration[a]
Cadmium	0.18	0.56	1.8	5.9	1.3
Mercury	0.03	0.08	0.3	0.8	0.2
Copper	2.9	9.0	29	96	25
Lead	3.0	9.4	30	101	15
Zinc	7.6	24	76	256	49
Chromium	3.0	9.4	30	101	24
Nickel	0.48	1.5	4.8	16	31
Total PCBs	0.02	0.05	0.17	0.6	0.001
Total PAHs	0.03	0.11	0.33	1.4	0.05
Total organic carbon (%)	0.04	0.14	0.43	1.5	1.0

[a]Elemental concentrations are from Grieg and Wenzloff (1977) for analyses of sediments below the 106-mile site and southwest of it. Except for cadmium they are lower than concentrations in deep-sea clays reported on a carbonate-free basis (Riley and Chester 1971). Sediments in the slope water region contain about 40% clay and 40% calcium carbonate (Rowe and Clifford 1978). PCB value is from Harvey and Steinhauer (1976b). PAH value (three-ring and larger) is calculated from Laflamme and Hites (1978). Total organic carbon concentration is from Rowe and Clifford (1978).

points in the four-dimensional history, including time, of dispersing waste plumes. High-frequency (20−200 kHz) acoustic sensors have therefore been used to continuously record vertical profiles of acoustic backscatter intensity (Proni and Hansen 1981; Orr and Hess 1978; Orr and Baxter 1983). In cases of sludge dumping this technique has shown increases in backscatter below pycnoclines. Orr and Baxter (1983) studied a sewage sludge dump at the 106-mile site which occurred at a discharge rate of 700 $m^3 \cdot km^{-1}$ during the month of July. This is the closest approximation to the proposed dumping we have discussed in this paper. The backscatter was limited to the mixed layer (26 m) except for an indication of an increase at 60 m. A single set of discrete water samples was collected 5 h after that dump (Kester et al. 1981b). Sludge was evident in the mixed layer as increases in concentrations of iron, cadmium, copper, and total organic carbon. Over the depths of 44−49 m there was an observed elevation in iron and total organic carbon. This indicates some descent of sludge.

Existing data on sludge dispersion, therefore, is at some variance with our restricting it to the mixed layer, except for individual particle settling. There are isolated and sketchy data to the contrary. No observations have been made on sludges dumped at 80 $m^3 \cdot km^{-1}$, the rate at which industrial waste dumping has occurred at the 106-mile site (O'Connor and Park 1982).

Acoustic sensing techniques have shown maxima in backscatter intensity at pycnocline depths. This is sometimes perceived to mean that waste particles settle through the mixed layer and accumulate at density gradients. Such an effect could be due to convective sinking of waste parcels with the sinking mass collapsing along pycnoclines, similar to rising plumes of pipeline-discharged (100:1 diluted) sewage which do collapse at pycnoclines (Jackson et al. 1979). However, barge-dumped wastes which have yielded acoustic signatures are either lighter than seawater (sewage sludges) or are discharged slowly enough for initial dilution to have nullified density differences between waste and seawater.

Acoustic backscatter intensity profiles cannot be readily converted to particle concentrations. These are functions of acoustic power and frequency and four unquantified properties of suspended solids: particle concentration, compressibility, density, and radius to the sixth or eighth power (Orr and Baxter 1983). Acoustic sensing has indicated pycnocline accumulation for particulate hydrous ferric oxide flocs which form upon disposal of acid-iron waste (Orr and Baxter 1983). Yet, vertical profiles of iron concentration (Brown et al. 1983) are consistent with our assumption of vertical homogeneity in the mixed layer. In principle, a few large particles whose descent is slowed at a pycnocline can create a maximum in backscatter intensity without there being a significant change in mass of waste per unit volume of seawater.

Particle descent will slow at pycnoclines, since ambient density (σ_t) increases, though the change (e.g. 5 σ_t) is small relative to particle densities. However, a decreased descent velocity is not equivalent to accumulation. The physical problem in rationalizing accumulation is that if particles fall fast enough not to be distributed through the mixed layer by turbulent diffusion, why should they stop sinking in a pycnocline where turbulence is decreased? While no pycnocline accumulation was observed with discharges of fine sediment in tests of deep ocean mining, Ichiye and Carnes (1981) approached the problem theoretically. Accumulation could be modeled if water rises from the pycnocline at a velocity near that of particle settling. This "Ekman pumping" occurs in response to wind having created a surface water divergence and can theoretically have a magnitude of the order of 10^{-3} $cm \cdot s^{-1}$, a velocity well within the range of sludge settling speeds (Table 3). However, such a mechanism, since it is wind

dependent, can apply only episodically. We do not include the base of the mixed layer in any special way in our description of the distribution of sludge.

Biological Effects

The distribution we have projected indicates contamination over a 60-km-wide swath beyond the edge of the continental shelf between the 106-mile site and the Gulf Stream off Cape Hatteras and a benthic accumulation of contaminants. The water column contamination would reach steady state about 30 d after the initiation of dumping. Benthic accumulation will continue as long as dumping does, being 10 times higher after 100 yr than after 1 yr. We have not considered water quality changes between the mixed layer and seafloor. Such changes will be much less than in the mixed layer because contaminants will be distributed over a greater vertical range. Also, for some elements, copper, zinc, nickel, and cadmium, there are nutrientlike concentration increases with depth (Bruland 1980). The depth dependence of zinc concentration is rather large, and while it could be a tracer of sludge in a 20-m-thick mixed layer, it would not be so indicative if constrained to a similar vertical range below the mixed layer.

We consider two classes of biological effects. One is contamination of marine organisms, including commercially caught fish in which case concern is for the quality of seafood eaten by humans. The other is change in the size or speciation of biological communities which would be of concern in itself and especially so if it resulted in stock decreases of valuable fishery resources.

Seafood Contamination

No commercial fishing is routinely done in slope waters; it is limited primarily to the area shoreward of the continental shelf break. It may extend seaward on those occasions when the shelf water/slope water front is itself seaward of the shelf break (Ingham 1981). Species taken at the shelf break during summer include squid (*Loligo peali* and *Illex illecebrosus*) (Kolator and Long 1979), American lobster (*Homarus americanus*), American shad (*Alosa sapidissima*), tilefish (*Lopholatilus chamaeleonticeps* and *Caulolatilus microps*), tuna (*Thunnus thynnus*), and marlin (*Tetrapturus albidus*) (Ray et al. 1980). Lobster and tilefish are benthic creatures limited geographically to the shelf, shad are primarily taken north of the 106-mile site and into Canadian waters, tuna and marlin have a wide migratory range, and squid migrate into and out of the mixed layer. In all cases, these fish would have limited exposure to contaminated water. During winter, these species are joined by black sea bass (*Centropristis striata*), scup (*Stenotomus chrysops*), Atlantic mackerel (*Scomber scombrus*), silver (*Merluccius bilinearis*) and red hake (*Urophycis chuss*), and summer flounder (*Paralichthys dentatus*). When within the contaminated zone these fishes would be exposed to concentrations at least 5 times less than those shown in Table 2 because of the deeper winter mixed layer.

Accumulation of contaminants is a process which depends on time, concentration, and chemical form of contaminant (e.g. Engel et al. 1981). The simplest way to assess seafood contamination in this discussion will be to assume that all sludge components are in dissolved, not particulate, form, in equilibrium with their ambient counterparts (if they exist), and to assume, as is implicit in Table 2, that all sludge is constrained to the upper 20 m. These assumptions lead to the conclusion that if fish were permanent residents of the contaminated zone their body burden levels of elements would increase by the ratios shown in the last column of Table 2. With these oversimplifying and maximizing assumptions we can derive somewhat meaningful levels of seafood contamination for lead and PCBs. Settle and Patterson (1980) report the only valid measurement of lead in fish tissue to be 0.3 ng·g wet wt^{-1}; increasing it by a factor of 26 yields a concentration of 8 ng·g^{-1}. Settle and Patterson (1980) indicate that tuna now in the marketplace contains 7−1400 ng lead·g^{-1} depending on whether cans are soldered, so our calculated contamination puts lead in seafood at the low end of what is now available. Again, ignoring the fact that of the total PCB in sludge, 75% is in the tetra- or penta-chloro form (MacLeod et al. 1981) rather than the more insoluble and lipophilic hexachloro compound, we use the bioaccumulation factor of 10^6 (Chiou et al. 1977) to conclude a PCB concentration in fish of 1.3 μg·g wet wt^{-1}. This is less than the U.S. Food and Drug Administration proposed limit of 2 μg·g^{-1} for seafood.

We have not considered microbial contamination of seawater or fish. Such contamination is certainly of concern in coastal areas where humans could be directly exposed to pathogenic microbes and has caused the closing of commercial shellfishing areas (Stanford et al. 1981). However, on the assumption that fin fish are not eaten raw, the U.S. Food and Drug Administration does not examine such organisms for bacterial contamination. There is some evidence that sewage-derived microorganisms would survive longer in the deep sea than in coastal or productive surface waters (Baross et al. 1975). This could imply a contamination of deep ocean benthos similar to that now occurring at coastal sludge discharge areas. However, that would have no public health consequences.

Planktonic Responses

Within the mixed layer, planktonic organisms will be constantly exposed to sludge-derived contamination. Estimates of sludge toxicity can be made on the basis of LC50 or EC50 concentrations which are periodically reported by municipalities now dumping sludge in the New York Bight (Table 5). The very low toxicity toward *Skeletonema costatum* reported for 1980 will be discounted, since it appears improbable that the organisms would suffer only a 50% growth reduction when exposed to a 20 000 mg·kg^{-1} suspended load corresponding to a twofold dilution of sludge. In 1980, either a very hardy strain of *S. costatum* must have been used or solids were removed from sludge prior to testing. Accepting the 1978 data as correct, since for 1978 and 1980 there is reasonable agreement for toxicity toward test animals, indicates that sludge diluted by 5×10^5 would be 1700 times more dilute than the lowest average LC50 or EC50 concentration. It could be assumed that sludge at such a dilution would not affect plankton in the ocean.

However, there are indications that even if the laboratory

TABLE 5. Short-term acute toxicity test results for New York/New Jersey sludges.

Test organism	Concentrations ($\mu L \cdot L^{-1}$) yielding a 50% die-off (LC50) or 50% growth reduction (EC50) over 96 h[a]			Dilution factor at average concentration[b]
	Average	Range over average	Total range	
S. costatum				
1978	3325	800–9000	50–36000	300
1980	457000	395000–500000	325000–925000	2
M. menidia				
1978	13300	5900–22000	3400–52500	77
1980	13000	7700–23000	3850–52000	75
M. bahia				
1978	11000	3900–8100	1920–45000	91
1980	6200	4500–17250	3000–37500	162

[a]For 1978, P. Anderson (USEPA Region II, personal communication) has summarized the results for eight dumping permittees. That data has been averaged after omitting the high and low concentrations. For 1980, two monthly analyses reports of 15 permittees were obtained and the lower concentration chosen. From the resulting list of 15 concentrations, high and low values were excluded and averages were calculated.

[b]For comparison, the dilution factor of sludge in contaminated zone is 500000 (Table 2).

response of *S. costatum* is representative of coastal phytoplankton, open ocean plankton may be more sensitive. Murphy and Belastock (1980) have demonstrated that contaminant responses of a particular phytoplankton species vary widely with the strain or isolate of that species. Open ocean isolates were more sensitive than their analogs from contaminated coastal waters. To our knowledge, open ocean phytoplankton have not been tested against sludge.

Data on the toxicity of individual sludge components to phytoplankton indicate that among xenobiotic compounds, PCBs appear to be particularly phytotoxic relative to other chlorinated compounds (Biggs et al. 1979) or to hydrocarbons (data in Neff 1979). However, the lowest concentration of PCBs observed to affect phytoplankton, 1000 $ng \cdot kg^{-1}$ (O'Connors et al. 1979), is 500 times greater than the sludge-amended concentration shown in Table 2. If there is a phytoplankton response to sludge it will probably be due to its trace element content.

The sensitivity of phytoplankton to trace metals is beginning to be studied not only from the point of view of contamination but also as it may control natural cycles of the size and composition of phytoplankton communities (Huntsman and Sunda 1981). Recent work has shown that if the same precautions taken for trace element sampling are also applied to biological work, species can be cultured which previously could not be (Rueter et al. 1979). To date, it appears that among the normally occurring trace elements, copper is the most effective in controlling phytoplankton growth. Rueter et al. (1979) found decreases in productivity of an open ocean species with copper additions as low as 690 $ng \cdot kg^{-1}$. Sunda and Ferguson (1983) found copper additions of 130–1300 $ng \cdot kg^{-1}$ to decrease rates of amino acid uptake by marine bacteria. The lowest addition was effective toward open ocean organisms, while the higher addition was needed to begin to affect coastal systems. Since it is metal activity (Sunda and Guillard 1976) rather than concentration which is of biological interest, it is important to know the rate of dissolution of metals from sludge. Morel and Schiff (1980) in an extensive discussion of coastal discharges of sewage effluents consider this point in detail. Available data (Rohatgi and Chen 1975) indicate that less than 10% of sludge copper would be dissolved in 20 d.

There is no firm basis on which to conclude that there would be a phytoplankton response to sludge disposal at the 106-mile site. However, trace elements, alone or in combination, may control the speciation of phytoplankton communities (Morel and Schiff 1980; Huntsman and Sunda 1981). If sludge is dumped it would be worthwhile, in the context of chemical sampling, to determine the composition of phytoplankton communities in and out of contaminated water downstream of the 106-mile site.

There are no data on zooplankton responses to New York/New Jersey sludges, though from Table 5 it might be concluded that sludge is more toxic to phytoplankton than to animals. There would likely be no significant zooplankton mortality from sludge dumping, but as Capuzzo and Lancaster (1983) point out, zooplankton do suffer a loss of fecundity at contaminant concentrations lower than acutely toxic ones. Again, if sludge is dumped, field measurements of zooplankton fecundity could be made.

Benthic Effects

While dissolution of sludge contaminants would tend to increase biological responses in the water column, the benthic contamination detailed in Table 4 would decrease. It would decrease also if there is a partitioning of sludge components among particles on the basis of specific surface area which would diminish their concentration in the faster settling, larger particle fraction. We will attempt to assess benthic biological effects on the basis of the contamination shown in Table 4 which would apply after 100 yr of dumping.

There is no coastal analog of this type of contamination. In areas where sludge is now evident in sediment (Bascom et al. 1981; Stanford et al. 1981) there are large increases in trace element levels, changes in sediment texture, and near bottom

oxygen depletion. None of these changes would occur if our description of sludge distribution is correct. A benthic response would appear to be limited to being due to relatively large increases in xenobiotic compound concentrations.

Our discussion of xenobiotic compounds is restricted to PCBs and PAHs because they constitute the bulk of such compounds identified in sludge (MacLeod et al. 1981). Other identified compounds include chlorinated pesticides and their metabolites (*trans*-Nonachlor and *p,p'*-DDE at 0.02 $\mu g \cdot g$ wet wt^{-1}; others below quantification limit), alkyl benzenes, chlorinated benzenes, and benzothiophenes (MacLeod et al. 1981). It is recognized that a fuller assessment of biological effects would include consideration of these and, probably equally or more importantly, unidentified xenobiotic compounds.

Near a sludge outfall off southern California, Bascom et al. (1981) reported a decrease in the infaunal trophic index (a measure of benthic communities) within an area where PCB concentrations exceed 1 $\mu g \cdot g$ dry wt^{-1}. Though other sediment changes have occurred within the same area and nothing can be directly attributed to a single contaminant, we have calculated that PCB concentration is more than 5 times the maximum after 100 yr.

Data of Laflamme and Hites (1978) indicate a total PAH level of 0.54 $\mu g \cdot g$ dry wt^{-1} in Gulf of Maine sediments which presumably harbor a normal benthic community. This is 1.4 times the maximum concentration, shown in Table 4, of 0.38 $\mu g \cdot g^{-1}$. Malins et al. (1980) in a comprehensive study of Puget Sound found apparently normal benthic communities in sediments containing more than 0.4 μg PAHs $\cdot g^{-1}$. They also observed degraded communities in sediments with lower PAH levels, the difficulty being that PAHs were not the only contaminant present in any case.

Although bioaccumulation of xenobiotics by deep-sea organisms is not a public health hazard, it should be examined as a possible prelude to ecological effects. Nimmo et al. (1971) exposed crabs to sediments spiked with 3–5 μg Aroclor 1254 $\cdot g^{-1}$; their results would indicate that epifaunal crustacea living on sediment containing 0.2 μg PCB $\cdot g$ dry wt^{-1} would contain about 0.2 μg PCB $\cdot g$ wet wt^{-1}. Bascom et al. (1981) report that benthic fishes near a sewage sludge outfall had PCB body burdens about equal to the concentrations in sediments. Fowler et al. (1978) spiked sediments which were "normally" 0.1 μg PCB $\cdot g^{-1}$ to levels of 0.7–80 $\mu g \cdot g^{-1}$. Their results indicate that polycheate worms living in sediment containing 0.2 μg PCB $\cdot g$ dry wt^{-1} would equilibrate at levels of 0.6–0.8 μg PCB $\cdot g$ dry wt^{-1} in tissues. On the basis of these data it may be estimated that benthic organisms associated with deep-sea sediments containing 0.2 μg PCB $\cdot g$ dry wt^{-1} would accumulate PCBs to levels of 0.2–0.8 $\mu g \cdot g$ dry wt^{-1}, the lower value applying to fish and the higher to infaunal worms. There are no data correlating PCB body burdens with physiological responses. Sherwood et al. (1978) on the basis of field data collected in diverse areas were not able to ascribe an etiological relationship between fin-rot disease and body burden levels of PCBs but tentatively concluded that if body burdens exceeded 0.1 $\mu g \cdot g$ wet wt^{-1} (about 0.5 $\mu g \cdot g$ wet wt^{-1}) fin-rot may be present in the population.

While PCB body burdens of organisms associated with sediment may equal or exceed PCB concentrations in sediment, the reverse applies for PAH compounds (Neff 1979). However, as Varanasi and Gmur (1981) demonstrated, the metabolism of PAH compounds to more soluble, excretable, and toxic compounds within organisms could mask the true extent of bioaccumulation. Nevertheless, available data on benthic effects from xenobiotic contamination, as tentative as they are, do not imply that the concentrations we have calculated to pertain after 100 yr would cause negative effects on the health of individual organisms or the stability of populations.

Summary

This first-order exercise on projecting consequences of dumping sewage sludge at the 106-mile site serves the purposes of indicating information needed to strengthen the projections and identifying field measurements which would be useful if sludge actually is dumped.

There is no information on settling velocities of New York/New Jersey sludges and no empirical data on the influence of natural or barge-induced turbulence on particle flocculation and therefore sinking rates. These data are needed to more realistically project sludge fluxes to the seafloor. If New York/New Jersey sludges are dewatered prior to transport, the relevant information would be for the settling rate distribution of sludges which are initially concentrated and then extensively diluted in barge-induced turbulence. Better approximations could be made for horizontal dispersion in the deep ocean by analysis of current velocity variations in Site-D data as was done by Jackson et al. (1979) for current meter data off southern California.

If sludge is actually discharged on a routine basis, our hypothesized distribution could be tested. Chemical analyses for sludge in the mixed layer downstream of the 106-mile site could be made, using the same precautions as required for "clean" seawater. The phytoplankton speciation and zooplankton fecundity could be compared between contaminated and noncontaminated waters. Sediment traps could be deployed to measure the horizontal distribution and flux of settling sludge.

An alternative dumping strategy which would eliminate consideration for surface water contamination would be to discharge sludge from barges through long pipes extending below the mixed layer. In this case there would be considerably less initial dilution and therefore faster settling of particles. Depending on the bulk density of the sludge (i.e. whether or not it is dewatered) a bolus of sludge would either rise or sink. The depth at which it reaches neutral buoyancy and collapses would have to be known and the subsequent settling distribution identified. This could entail a very fast settling of a large fraction of the sludge with a resulting benthic accumulation which could have ecological consequences.

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The Role of Zooplankton in the Accumulation and Deposition of DuPont Edgemoor Waste (an Acid-Iron Waste) at a Deepwater Dumpsite in the Northwest Atlantic[1]

JUDITH M. CAPUZZO

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

CAPUZZO, J. M. 1983. The role of zooplankton in the accumulation and deposition of DuPont Edgemoor waste (an acid-iron waste) at a deepwater dumpsite in the northwest Atlantic. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 242–247.

DuPont Edgemoor waste derived from titanium dioxide production is a highly acidic solution of ferric chloride containing relatively high levels of several trace metals including Cr, V, Pb, Ni, Cu, and Cd. Approximately 3×10^5 t·yr^{-1} are dumped at Deepwater Dumpsite 106, ~160 km southeast of Ambrose Light, New York. Chemical dispersion studies at the dumpsite indicate that ferric oxide precipitates in the waste plume and that other trace metals may become associated with this particulate phase. Ingestion of this particulate phase by copepods is a significant route of uptake for the waste-derived metals in the laboratory. Accumulation of the various metals by exposed copepods ranged from 10.8% above control values for Fe to 54.7% for Cu. The ratios of the various trace metals relative to Fe were only slightly enhanced in exposed copepods in comparison with control copepods but 1 to 2 orders of magnitude higher than the metal ratios of a 10^5 waste dilution. Enhancement of metal concentrations in fecal pellets produced by exposed copepods ranged from 25.0% above control values for Fe to 60.3% for Cu. Metal deposition through fecal pellet production appears to be an effective means of depurating Fe, Pb, Ni, and Cu by copepods exposed to Edgemoor waste but not for Cd, which could not be detected in fecal pellets. The greater density of fecal pellets compared with the ferric oxide particles could result in a more rapid sinking rate of waste-derived metals to the deep ocean. The flux of waste-derived metals through zooplankton biomass and the contribution of zooplankton in the biogeochemical cycling of metals at Deepwater Dumpsite 106 suggests that biological processes may be as important as advective processes in determining the fate of waste-derived metals.

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Les eaux usées de DuPont Edgemoor dérivées de la production de bioxyde de titanium sont une solution fortement acide de chlorure ferrique contenant des niveaux relativement élevés de plusieurs métaux en traces, dont Cr, V, Pb, Ni, Cu et Cd. Au site d'immersion en profondeur 106, à environ 160 km au sud-est du phare Ambrose, New York, sont déversées environ 3×10^5 t·an^{-1}. Des études de dispersion chimique à ce site indiquent que les précipités d'oxyde ferrique dans le panache d'eaux usées et les autres métaux en traces peuvent être associés à cette phase particulaire. L'ingestion de cette dernière par les copépodes est une importante voie d'assimilation en laboratoire des métaux dérivés de ces déchets. L'accumulation des divers métaux dans les copépodes exposés varie de 10,8 % au-delà des valeurs témoins dans le cas de Fe à 54,7 % dans celui de Cu. Les rapports entre les divers métaux en traces et Fe n'augmentent que légèrement chez des copépodes exposés comparativement aux témoins, mais sont supérieurs de 1 ou 2 facteurs aux rapports des métaux avec dilution de 10^5 des eaux usées. L'élévation des concentrations de métaux dans les boulettes fécales produites par des copépodes exposés varie de 25,0 % au-delà des valeurs témoins pour Fe à 60,3 % pour Cu. Il semble que la déposition des métaux par production de boulettes fécales soit un moyen efficace de dépuration de Fe, Pb, Ni et Cu par les copépodes exposés aux eaux usées de Edgemoor. Ce n'est toutefois pas le cas pour Cd, qui ne peut être détecté dans les boulettes fécales. Il se peut qu'une plus forte densité de boulettes fécales par rapport aux particules d'oxyde ferrique résulte en un taux de sédimentation plus rapide des métaux dérivés des eaux usées dans les profondeurs océaniques. Le flux de ces métaux dans la biomasse zooplanctonique et la contribution du zooplancton au recyclage biogéochimique des

[1]Woods Hole Oceanographic Institution Contribution No. 4993. This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6866)
Imprimé au Canada (J6866)

métaux au site d'immersion 106 donnent à croire que, dans la détermination du sort des métaux dérivés des eaux usées, les processus biologiques sont aussi importants que les processus advectifs.

Received March 19, 1982
Accepted October 29, 1982

Reçu le 19 mars 1982
Accepté le 29 octobre 1982

OCEAN dumping of industrial wastes provides an alternative to land-based disposal of toxic materials, but the impact of waste disposal on the marine ecosystem is not well understood. Because of their fragile nature and ecological importance in marine food chains, the sensitivity of plankton populations to industrial wastes is a problem of great concern. Exposure to industrial wastes may result in either reduced plankton biomass at several trophic levels or accumulation and transfer of toxic materials from one trophic level to another; either response may lead to significant imbalances or alterations in food chain dynamics.

Deepwater Dumpsite 106 (DWD 106) is located on the continental slope of the northwest Atlantic Ocean, ~160 km southeast of the Ambrose Light, New York, and wastes from the DuPont Edgemoor plant have been dumped at this site for several years. The physical and chemical characteristics of this and other wastes and their dispersal at sea have been investigated since dumping was initiated (Csanady 1981; Kester et al. 1981; Orr and Hess 1978). DuPont Edgemoor waste is derived from titanium dioxide production and is a highly acidic solution of ferric chloride containing several trace metals including Cr, Cu, V, Cd, Ni, and Pb (Csanady et al. 1979). Upon mixing of the acid-iron waste with seawater, hydrous ferric oxide particles are precipitated (Kester et al. 1981). Using acoustic backscattering techniques, Orr et al. (1979) observed accumulation of these particles within the maximum density gradient at a depth of 15–30 m during the summer and at greater depths during winter months. Layering of particles along the thermocline persisted for several hours and horizontal dispersion of the waste was accomplished by internal waves. Kester et al. (1981) demonstrated that the ferric oxide particles could scavenge other toxic metals (such as Cu, Cd, and Pb) from the waste plume and provided an adequate index of waste dilution. Initial dilution by a factor of 10^4 (100 ppm) occurred within 0.5 h, followed by slower dilution to 10^5–10^6 (1–10 ppm) after 27 h. Fe and Pb concentrations were highly correlated with dispersion of the particulate phase; Cu and Cd concentrations, however, were less associated with particles and a slower dispersion rate was evident.

The persistence of waste in surface waters for at least several days postdumping increases the availability of waste-derived metals to planktonic organisms. DuPont Edgemoor waste is acutely toxic to marine zooplankton at dilutions of 10^5 and Capuzzo and Lancaster (1983) have reported 96-h LC_{50} values at dilutions of 10^4 for several species of marine copepods. Uptake of waste-derived metals, both soluble and particulate phases, by zooplankton exposed to sublethal concentrations of waste may influence the distribution and flux of metals within surface waters affected by waste plumes. The objective of this study was to determine the uptake, accumulation, and deposition of waste-derived metals by the marine copepod *Centropages typicus* in an attempt to elucidate the potential role of zooplankton in the biogeochemical cycling of metals at DWD 106.

Materials and Methods

Collections of the copepod *C. typicus* were made by plankton tows at a depth of 10 m off Gay Head in Vineyard Sound, MA, and off the Elizabeth Islands in Buzzards Bay, MA. These water masses receive no industrial waste inputs and are typical of "clean" nearshore areas. Adult males and females were isolated for laboratory culture and maintained in 8-L carboys at a density of 100 copepods·L^{-1} at 20–22°C and 30–31‰ salinity under constant illumination. Filtered seawater from Vineyard Sound, MA, was changed every 3rd d and copepods were fed a mixed algal diet of *Isochrysis* and *Phaeodactylum* (1×10^5 cells·mL^{-1}) and newly hatched *Artemia* nauplii (Brazilian strain, Aquafauna, Inc.) and were used in bioassays only as adults. Further details of culture procedures are presented in Capuzzo and Lancaster (1983).

To determine the accumulation of the metal components of DuPont Edgemoor waste in zooplankton biomass, samples of 1000 specimens of adult, first-generation *Centropages* were exposed to a 10^5 seawater – Edgemoor waste dilution (10 ppm) at 20°C for 96 h in 12-L carboys. Metal composition (Fe, Pb, Ni, Cu, Cd, and V) of exposed copepods was compared with that of control copepods maintained under similar conditions. After the end of the exposure period, copepods were collected on a 100-μm Nitex® screen, rinsed with distilled water for 30 s, dried at 70°C for 24 h, and weighed. After weighing, the samples were ashed at 550°C to remove chitinous and organic matter and extracted in nitric and perchloric acids according to the extraction procedures of Polikarpov et al. (1979). Concentrations of the various metals were determined by atomic absorption spectrophotometry using a Perkin Elmer AA with a graphite furnace attachment. Fecal pellets were siphoned from the bottom of each carboy, collected on a 35-μm Nitex® screen to remove nonfecal particles, rinsed with distilled water, and dried. Fecal pellet collections were pooled from six carboys for each replicate. After drying, fecal pellets from both exposed and control copepods were extracted with nitric acid without ashing and assayed for metal composition. Three replicate samples of copepods and pooled fecal pellets were assayed for metal concentrations; analytical measurements were made in duplicate. Trace metal concentrations of seawater–waste mixtures were measured at the beginning and end of each experiment using a modification of the technique of Boyle and Edmond (1977), as described by Kester et al. (1981).

Particle distribution of the seawater–waste mixtures were determined with a Coulter counter (model TA-II) using a 140-μm aperture. Visual observations of particle ingestion by

TABLE 1. Metal composition of DuPont Edgemoor waste (4-79).

Metal	Concentration ($mg \cdot kg^{-1}$)	Ratio to Fe
Fe	13 000	1
V[a]	75	5.8×10^{-3}
Cr	60	4.6×10^{-3}
Pb	11	8.5×10^{-4}
Ni	7	5.4×10^{-4}
Cu	1.25	9.6×10^{-5}
Cd	0.19	1.5×10^{-5}

[a]V analysis by N_2O flame; all others by air–acetylene flame.

Centropages and measurements of size and settling velocity of fecal pellets were also made.

Results

Iron was the major constituent detected in DuPont Edgemoor waste, with lesser amounts of Cr, Pb, V, Ni, Cu, and Cd (Table 1). The density of the waste was 1.16 $g \cdot cm^{-3}$ and the pH was 0.01. When diluted with seawater by a factor of 10^5, a particulate phase (hydrous ferric oxide) was formed. The concentration of particles of the 10^5 seawater–waste dilution was $3.1 \times 10^3 \cdot mL^{-1}$, with 99% of the particles ≤ 15 μm; the pH of this waste dilution was 7.9 compared with 8.0 for the control seawater.

The increase in Fe content in the seawater–waste dilution was in excess of 1 order of magnitude above ambient seawater levels (Table 2); enhancement of the other metals was on the order of 1.5- to 3.5-fold increases. The ratios of Pb, Ni, Cu, and Cd relative to Fe were greater in the seawater–waste dilution than in the undiluted waste, suggesting that these metals might, at least partially, be associated with the iron oxide particles. Ingestion of this particulate phase was observed among actively feeding copepods.

Enhancement of trace metals in the biomass of *C. typicus* exposed for 96 h to 10 ppm Edgemoor waste did not follow the same pattern as seawater concentrations. Although Fe was the major trace metal constituent measured in both control and exposed copepods, an increase of only 10.8% was detected in exposed copepods (Table 3). Increased levels of the other trace metals ranged from 30.0 to 54.7% above control levels. The ratios of the various trace metals relative to Fe were only slightly enhanced in exposed copepods in comparison with control copepods but 1 to 2 orders of magnitude higher than the metal ratios for the seawater–waste dilution. Since some loss of Cd may be apparent at ashing temperatures in excess of 450°C, Cd values in copepod biomass may be underestimated. The values reported here, however, are consistent with those reported for zooplankton biomass by other investigators (Polikarpov et al. 1979; Davies 1978).

Metal concentrations were higher in fecal pellets than in copepod biomass for both control and exposed groups (Table 4), and ingested phytoplankton was presumably a major source of metal intake and deposition. Enhancement of metal concentrations in fecal pellets produced by exposed copepods ranged from 25.0 to 60.3% above control values. Cd was not detectable in fecal pellets produced by either group of copepods. The ratios of Pb, Ni, and Cu relative to Fe were slightly enhanced in fecal pellets produced by exposed copepods in comparison with those produced by control copepods; ratios of Pb, Ni, and Cu to Fe were higher in fecal pellets of exposed copepods than in the seawater–waste dilution but generally lower than ratios in copepod biomass. Except for Fe, the magnification factors for the various metals in copepod biomass and fecal pellets were similar in the control and exposed groups (Table 5).

Although fecal pellet production was similar in both groups of copepods (Table 6), only 57% of the fecal pellets of exposed copepods was metabolically derived from unassimilated food due to a reduction in feeding rate with exposure to 10 ppm Edgemoor waste (Capuzzo and Lancaster 1983). The remainder of the fecal pellets produced by exposed copepods was partially derived from unassimilated ferric oxide particles, as evidenced by the yellowish orange appearance of some of the fecal pellets.

The fecal pellets produced by both groups of copepods were cylindrical in shape with a volume of approximately 0.4×10^6 to 0.6×10^6 μm^3; the density of the fecal pellets was 1.25 $g \cdot cm^{-3}$, consistent with the findings of Komar et al. (1981). Settling velocity of fecal pellets was calculated according to the equation given by Komar et al. (1981) for cylindrical pellets and was equivalent to 6.9×10^{-2} $cm \cdot s^{-1}$ or 60 $m \cdot d^{-1}$.

The relative partitioning between copepod biomass and feces (Table 7) was diverse for each of the metals studied, suggesting both differential assimilation and depuration rates. The percentage of increased metal burden deposited as fecal

TABLE 2. Concentration of metals in seawater and 10^5 seawater – Edgemoor waste dilution (10 ppm). Means of three replicate samples, coefficient of variation ≤10%; analyzed by the Co coprecipitation method of Boyle and Edmond (1977). V concentration was below detectable limits and Cr was not extractable by this method.

Metal	Concentration ($\mu g \cdot kg^{-1}$)		Ratio to Fe	
	Seawater	Seawater–waste	Seawater	Seawater–waste
Fe	3.5	113.0	1	1
Pb	0.2	0.3	5.7×10^{-2}	2.7×10^{-3}
Ni	0.25	0.4	7.1×10^{-2}	3.5×10^{-3}
Cu	0.2	0.5	5.7×10^{-2}	4.4×10^{-3}
Cd	0.02	0.07	5.7×10^{-3}	6.2×10^{-4}

TABLE 3. Metal composition of *C. typicus* exposed to 10 ppm Edgemoor waste at 20°C for 96 h. Means of three replicate samples of 1000 animals each, ashed at 550°C and acid digested; coefficient of variation was ≤5% for Fe and Cu and ≤10% for Pb, Ni, and Cd.

Metal	Concentration ($\mu g \cdot g^{-1}$ dry wt)		% increase relative to control	Ratio to Fe	
	Control	Exposed		Control	Exposed
Fe	74.0	82.0	10.8	1	1
Pb	3.0	3.9	30.0	4.1×10^{-2}	4.8×10^{-2}
Ni	2.6	3.5	34.6	3.5×10^{-2}	4.3×10^{-2}
Cu	32.0	49.5	54.7	4.3×10^{-1}	6.0×10^{-1}
Cd	0.6	0.9	50.0	8.1×10^{-3}	1.1×10^{-2}

TABLE 4. Metal composition of fecal pellets collected from *C. typicus* exposed to 10 ppm Edgemoor waste at the end of the exposure period. Means of three replicate pooled samples, acid digested; coefficient of variation was ≤5% for Fe and Cu and ≤10% for Pb, Ni, and Cd.

Metal	Concentration ($\mu g \cdot g^{-1}$ dry wt)		% increase relative to control	Ratio to Fe	
	Control	Exposed		Control	Exposed
Fe	10 800	13 500	25.0	1	1
Pb	243	340	39.9	2.3×10^{-2}	2.5×10^{-2}
Ni	50	73	46.0	4.6×10^{-3}	5.4×10^{-3}
Cu	390	625	60.3	3.6×10^{-2}	4.6×10^{-2}
Cd	0.0	0.0	—	—	—

TABLE 5. Magnification factors for metal composition of *C. typicus* exposed to 10 ppm Edgemoor waste. Magnification factor = concentration in body or fecal pellets/concentration in seawater or 10 ppm waste.

Metal	Body		Fecal pellets	
	Control	Exposed	Control	Exposed
Fe	2.1×10^{4}	7.3×10^{2}	3.1×10^{6}	1.2×10^{5}
Pb	1.5×10^{4}	1.3×10^{4}	1.2×10^{6}	1.1×10^{6}
Ni	1.0×10^{4}	8.8×10^{3}	2.0×10^{5}	1.8×10^{5}
Cu	1.6×10^{5}	2.5×10^{5}	2.0×10^{6}	1.3×10^{6}
Cd	3.0×10^{4}	1.3×10^{4}	—	—

pellets ranged from 99.4% for Fe to 0.0% for Cd. Excretion of dissolved metal species is another potential route of depuration from copepod biomass but it was not investigated in this study.

Discussion

The role of zooplankton in the biogeochemical cycling of trace metals and organic compounds has been considered by some investigators to have a significant impact on the distribution and fate of these chemicals in the marine environment. The uptake of trace chemicals by zooplankton may occur through adsorption to body surfaces, water exchange at respiratory and feeding surfaces, and ingestion of food and detrital particles (Davies 1978); removal may occur through excretion and the production of particulate products such as eggs, molts, and fecal pellets (Davies 1978; Fowler 1977). The balance of these processes for individual trace chemicals, such as the trace metals investigated in the present study, may result in selective uptake, accumulation, and deposition by zooplankton.

Davies (1978) compiled the available literature (pre-1978) of heavy metal levels in marine zooplankton and attributed the wide range of concentrations detected to pollution gradients. The concentrations of Hg, Cu, Pb, and Zn in zooplankton biomass were considerably higher in plankton samples collected in nearshore areas than those collected from offshore areas of the north Atlantic Ocean (Windom 1972; Windom et al. 1973). High concentrations of Hg were also detected in zooplankton collected from other coastal areas receiving industrial effluents (Vucetic et al. 1974; Corral and Masso 1975; Skei et al. 1976). Although trace metal concentrations have been measured in zooplankton collected from a wide range of geographical locations, little attention has been given to increased accumulation associated with specific pollution problems.

Depuration of metals by zooplankton and incorporation into fecal pellets has been suggested by several investigators to be a major pathway of deposition of metals to the deep sea. Osterberg et al. (1963) were the first to suggest that incorporation of radionuclides into fecal pellets coupled with the rapid sinking rates of fecal pellets accelerated the rate of radionuclide deposition to the deep ocean. Lowman et al. (1971) estimated that 92% of radioactive iron as ^{55}Fe or ^{59}Fe was transported to the deep ocean by fecal pellets and other particulate products. Similar conclusions were drawn by

TABLE 6. Metal deposition (micrograms per kilogram of copepods per day) due to fecal pellet production by *C. typicus*. Fecal pellet production equivalent to 2.1 $\mu g \cdot d^{-1} \cdot copepod^{-1}$; dry weight of adult *C. typicus* equivalent to 37.5 μg.

Metal	Control	Exposed	
		Food-derived	Waste-derived
Fe	6.2×10^5	4.4×10^5	3.3×10^5
Pb	1.4×10^4	1.1×10^4	8.0×10^3
Ni	2.9×10^3	2.4×10^3	1.8×10^3
Cu	2.2×10^4	2.1×10^4	1.5×10^4

TABLE 7. Partitioning of metals by *C. typicus* exposed to 10 ppm Edgemoor waste.

Metal	Increase above control ($ng \cdot copepod^{-1} \cdot 96\ h^{-1}$)		% deposited as fecal pellets
	Body	Fecal pellets	
Fe	0.3	49.6	99.4
Pb	0.04	1.2	96.8
Ni	0.03	0.28	90.3
Cu	0.7	2.24	76.2
Cd	0.01	0.0	0.0

Kuenzler (1969) for Co and by Small and Fowler (1973) for Zn. Further evidence suggests that fecal pellet deposition may indeed be a primary factor controlling the residence time of metals in the marine environment (Cherry et al. 1978).

The availability, accumulation, and deposition of metals from an acid-iron waste by zooplankton were investigated in the present study, using the copepod *C. typicus* as a test species. Kester et al. (1981) characterized the dispersion of this waste in two phases: (1) a particulate phase where measurements of total suspended matter, total Fe, particulate Cu, Pb, and Cd, and total Pb were closely correlated and subject to rapid initial dilution, followed by a slower rate of dispersion, and (2) a dissolved phase where measurements of total Cu and Cd correlated with one another but were independent of the other parameters and resulted in a much slower dispersion rate. The independent variations of Cu and Cd relative to the other metals are attributed to their seawater chemistry where they are more associated with soluble inorganic and organic complexes (Engel et al. 1981) than particulate phases. Kester et al. (1981) estimated that approximately 50% of waste-derived Cu was in a particulate phase, whereas only a small percentage of Cd was measured as particles; Pb and Fe occurred primarily in particulate phases.

Using chemical dispersion data to predict pathways of metal uptake by *Centropages* in the present study, it is apparent that uptake of Fe and Pb is primarily through ingestion of particles, whereas uptake of Cu and Cd is most probably by a combination of diffusion and particle ingestion for Cu and primarily diffusion for Cd. Higher rates of accumulation relative to control values were observed for the latter two metals. Although Kester et al. (1981) did not investigate the partitioning of Ni in the waste plume, it was most probably associated with the particulate phase, as evidenced by its similarity to Pb in several aspects of the present study and an accumulation rate intermediate between Pb and Cu.

Concentrations of Fe, Pb, Ni, Cu, and Cd in control and exposed specimens of *Centropages* are within the ranges cited by Davies (1978) for marine zooplankton and are well below values measured for copepods collected in polluted areas. The removal of metals from zooplankton biomass through fecal pellet deposition is an effective means of metal depuration during short-term exposures to pollution conditions such as those defined in the present study. The high rate of incorporation of metals into fecal pellets, especially for particle-bound metals such as Fe, Pb, and Ni, would suggest that the hydrous ferric oxide particles are relatively nonpersistent in zooplankton biomass. Cd and to some extent Cu appear to be more persistent, presumably related to their mode of uptake.

The deposition of waste-derived metals in fecal pellets by marine copepods provides a means of rapid transport of the components of Edgemoor waste out of the mixed layer in the dumpsite area. Fowler (1977) suggested that zooplankton fecal pellets, because of their high rate of production and slow rate of decomposition, have the greatest potential for transporting metals to the deep ocean. The settling velocity of uningested ferric oxide particles is presumably quite slow. Orr et al. (1979) demonstrated some seasonal differences in dispersion of Edgemoor waste at DWD 106 but observed a general trend of initial rapid sinking of waste-derived particles at a rate of 1.0–5.8 $m \cdot min^{-1}$ for a period of ~20 min following waste discharge; further sinking was restricted by density gradients. Using Stoke's Law to predict the settling velocity of the dispersed particulate phase of Edgemoor waste, an average sized particle, 10–15 μm in diameter, would settle at a rate of only 0.1–0.15 $m \cdot d^{-1}$, almost 3 orders of magnitude slower than the fecal pellets measured in the present study.

Although the sinking rate of copepod fecal pellets is relatively high and the density of fecal pellets is sufficient so that their transport is not retarded at density gradients, at a sinking velocity of 60 $m \cdot d^{-1}$ fecal pellets would not reach the bottom of a 2000-m water column for 33.3 d. Small et al. (1979) suggested that because of slow settling velocities and reingestion, fecal pellets of small copepods were important in biogeochemical cycling and redistribution of elements in surface waters and were less important in the vertical flux of materials to the deep ocean. Fecal pellets produced by larger zooplankton forms, such as euphausiids, with sinking rates of 100–500 $m \cdot d^{-1}$ would be more important for rapid transport to the deep ocean. The fecal pellets produced by *Centropages* in the present study are intermediate in size and settling velocity and thus may contribute to both surface-water redistribution and deep-water flux.

The importance of zooplankton fecal pellets in the biogeochemical cycling of Edgemoor waste at DWD 106 has not been investigated under in situ field conditions. Field programs are needed to assess not only the toxic effects of discharged wastes on plankton populations but also the role of plankton in the cycling of wastes, as these may be as important as advective processes in determining the fate and dispersion of waste materials.

Acknowledgments

This research was supported by NOAA, Office of Marine Pollution

Assessment, under grant No. NA79AA-D-00027. The assistance of Bruce A. Lancaster for collection and maintenance of copepod cultures and Steven Manganini, Mark Dennett, and Rodman E. Taylor for chemical analyses is greatly appreciated.

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Eddy-Enhanced Dispersion of Ocean-Dumped Organic Waste at Deep Water Dumpsite - 106[1]

DENIS A. WIESENBURG[2] AND JAMES M. BROOKS

Department of Oceanography, Texas A&M University, College Station, TX 77843, USA

WIESENBURG, D. A., AND J. M. BROOKS. 1983. Eddy-enhanced dispersion of ocean-dumped organic waste at Deep Water Dumpsite - 106. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 248 – 261.

Volatile organic compounds (VOC) discharged into northwestern Atlantic slope waters at a deep ocean dumpsite were dispersed to background levels within 24 h. The main VOC (>85%) of the waste was toluene, with a large mercaptan component. Several trichlorobenzenes were present in trace amounts. Initial dilution from wake dispersion reduced the waste levels by a factor of 1300. Mixing processes and evaporative loss to the atmosphere further reduced surface water concentrations of VOC by a factor of 1000 in 9 h and to background levels within 24 h. The rapid loss of volatiles from the dumpsite waters results from the very volatile nature of the dumped material and physical mixing processes. The presence of the edge of a large, anticyclonic, warm-core Gulf Stream eddy (ring) in the dumpsite area probably increased local mixing processes which resulted in the rapid dispersion of the waste. The presence of the ring water in the dumpsite area could also account for the low background concentrations observed in the dumpsite.

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Les composés organiques volatiles (COV) déversés dans les eaux de pente de l'Atlantique nord-ouest à un site de déversement en eaux profonde sont dispersés et atteignent les niveaux de base en dedans de 24 h. Le principal COV (>85 %) des déchets est le toluène, en plus d'une forte proportion de mercaptan. Plusieurs trichlorobenzènes sont présents en traces. Une dilution initiale dans les eaux de sillage abaisse les niveaux de déchets d'un facteur 1 300. Les concentrations de COV dans les eaux de surface sont encore réduites par les processus de mélange et les pertes dans l'atmosphère par évaporation, d'un facteur 1 000 en 9 h et aux niveaux de base en dedans de 24 h. La nature très volatile du matériel déversé et les processus physiques de mélange sont responsables de sa rapide disparition dans les eaux du site de déversement. La présence d'un tourbillon à coeur chaud du Gulf Stream, anticyclonique et de grande étendue, effleurant le site de déversement, accentue probablement les processus de mélange locaux, causant une dispersion rapide des déchets. L'eau de ce tourbillon peut aussi expliquer les faibles concentrations de base qu'on y a observées.

Received March 19, 1982
Accepted November 22, 1982

Reçu le 19 mars 1982
Accepté le 22 novembre 1982

As industrialized society continues to grow, the quantity of waste materials produced increases proportionately. Much of this material is innocuous solid wastes or biodegradable products which can be safely disposed of in landfills or through sewage treatment processes. An increasing percentage of waste, however, is toxic industrial by-products which require more sophisticated disposal methods to keep them from reentering the biosphere in a harmful manner. An estimated 57 × 10^6 t of hazardous industrial waste was produced during 1980 in the United States alone.

Choices for waste disposal are limited. We can use the land upon which we live, the air we breathe, or the water, which is required by all life forms. The United States Environmental Protection Agency lists the various acceptable means for disposing of waste material as landfills, well injection, incineration, spread of materials over open ground, recycling of material for reuse, storage, or ocean dumping. Ocean dumping is allowed, with certain exceptions, only when there are no practical alternate locations and no methods of disposal or recycling are available which have less adverse

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Biological and Chemical Oceanography Branch, Oceanography Division, Naval Ocean Research and Development Activity, NSTL Station, MS, 39529, USA.

Printed in Canada (J6867)
Imprimé au Canada (J6867)

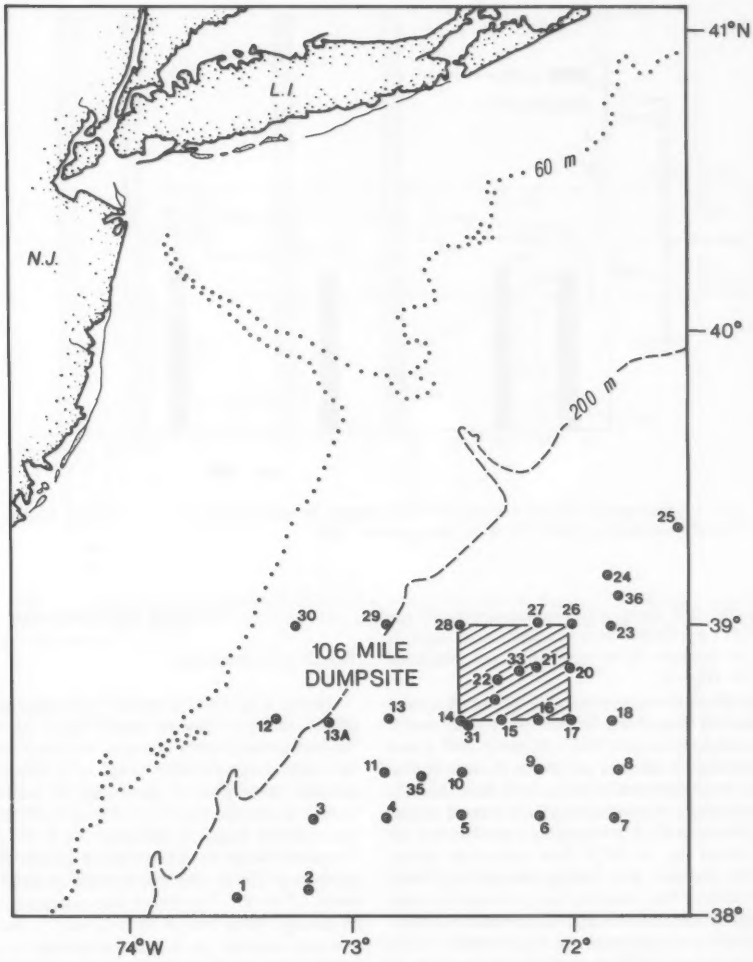

FIG. 1. Station map showing sampling locations during July 1980. The hatched area indicates the areal extent of DWD-106 off the northeast coast of the United States.

environmental impact or potential risk to other parts of the environment.

Ocean dumping of industrial wastes is a reality, however. The Middle Atlantic Bight has been used for many years to dispose of a variety of wastes (Anderson and Dewling 1981). Yet there is continued debate as to whether the ocean is a suitable waste repository to be managed (Goldberg 1981) or whether it is too fragile and important an environment to be used for such purposes (Kamlet 1981). Our ability to use the oceans as waste space is predicated upon our capacity to analyze the potential adverse effects of ocean dumping on the biota (Capuzzo 1981). Such studies must determine whether dumped materials are rapidly rendered harmless by the physical, chemical, or biological processes in the sea. This paper examines one particular discharge of industrial waste at an east coast United States offshore dumpsite, Deep Water Dumpsite - 106 (DWD-106), to ascertain the fate of volatile organic compounds (VOC) dumped there. Although the amount of ocean dumping in United States waters is decreasing overall, DWD-106 has received increasing amounts of industrial chemical waste in recent years.

The Study Area

Deep Water Dumpsite - 106 (DWD-106) has been used as a disposal area for industrial chemical waste for more than a

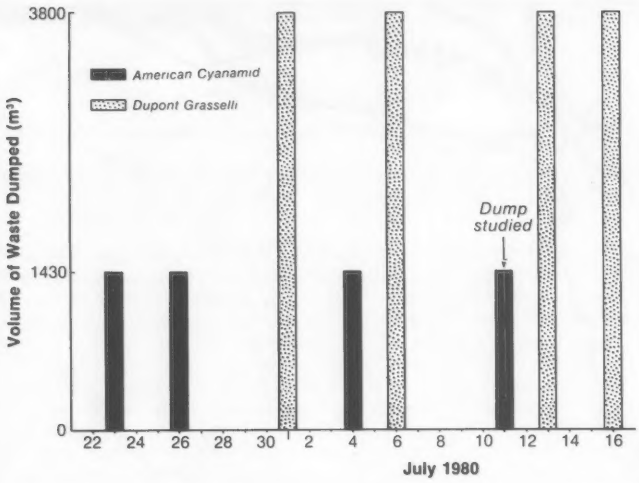

FIG. 2. Histograms showing volumes of waste dumped by American Cyanamid (black) and DuPont Grasselli (stippled) at DWD-106 during June and July 1980.

decade. The rectangular dump area, located about 195 km southeast of New York Harbor over the continental slope, is encompassed by latitude 38°40′–39°00′N and longitude 72°00′–72°30′W (Fig. 1).

The complex physical oceanography of the area has been discussed in detail by Bisagni and Kester (1981). They noted, as have others (e.g. Cresswell 1967; Csanady 1979) that DWD-106 is located in an area of strong oceanic frontal dynamics. The occurrence and movement of these oceanic fronts and the passage of anticyclonic Gulf Stream eddies (rings) through the area allow a variety of water types to be present at the dump site. In 1979, four warm-core eddies passed through the dumpsite area. During June and July 1980, between 8 and 85% of the dumpsite was covered by warm eddies, effectively displacing the slope water which normally occupies the dumpsite area (Bisagni and Kester 1981). These eddies have increased eddy diffusivities in their shear boundaries and may be important in dispersion of the ocean-dumped waste at DWD-106.

E. I. DuPont de Nemours and Company (Grasselli and Edge Moor plants) and American Cyanamid (Warner plant) are licensed by the United States Environmental Protection Agency to dispose of chemical waste at DWD-106. During June and July 1980, wastes were dumped at DWD-106 from the DuPont Grasselli and American Cyanamid plants (Fig. 2). The American Cyanamid waste was discharged from the tanker *Susan Frank* (1.4×10^6 L), while the DuPont wastes (3.8×10^6 L) were delivered in the barge *Sparkling Waters*. Ordinarily, the barge carries waste from both DuPont Grasselli and American Cyanamid Warner in separate compartments; however, the DuPont plant was not operating in late June 1980.

Methods and Materials

THE DUMP EXPERIMENT

During July 1980 a cruise was undertaken aboard the NOAA ship *Mt. Mitchell* (cruise RP-27-MI-80) to examine the background levels of waste at DWD-106 and to study the waste dispersion after dumping. A series of stations was sampled, most prior to the dump, to determine the background levels. On July 11, 1980, at 18:30 GMT, the tanker *Susan Frank* began discharging 1.4×10^6 L of American Cyanamid waste in a box-shaped pattern in the southeast quadrant of DWD-106. The forward speed of the tanker was about 1.7 $m \cdot s^{-1}$. The tanker was emptied in about 3 h, with an average dump rate of 7800 $L \cdot min^{-1}$. The discharge rate was not constant, as it was determined by the hydrostatic pressure head in the barge and pump pressure. This resulted in the waste initially forming patches, and not a single column, behind the tanker.

The purpose of this dump experiment was to examine the fate of the VOC in the discharge with time. It was thus imperative that the same water mass be tracked throughout the experiment. This was accomplished using two independent techniques. Two radar-reflecting buoys were deployed in the waste plume at the beginning of the experiment to track plume drift. The buoys were drogued at depths of 10 or 25 m and their positions were recorded relative to the ship by range and bearing every 15 min. The buoys moved to the north with a separation of a few hundred metres after 9 h. Expendable bathythermographs were also deployed during this experiment to track the depth of the mixed layer.

Continuous location of the plume was also facilitated by

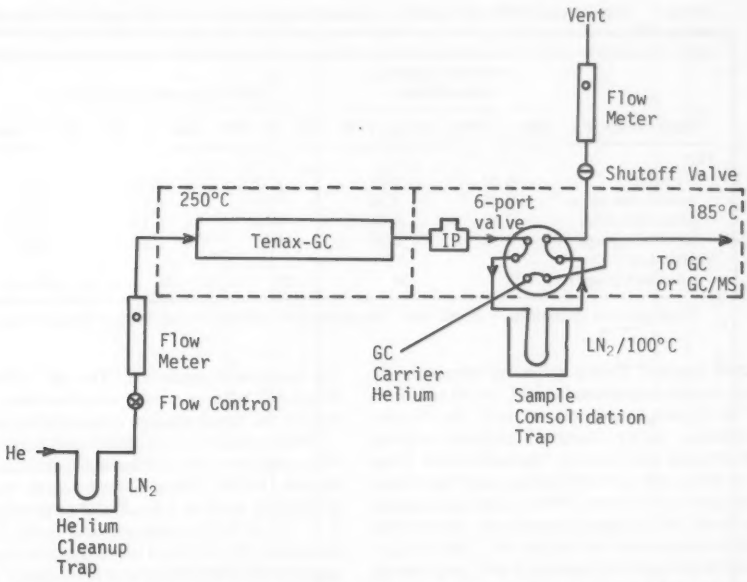

FIG. 3. Desorption system designed to remove adsorbed VOC from the Tenax-GC, consolidate them on a liquid nitrogen (LN_2) trap, and inject the sample as a plug onto a gas chromatographic column for separation and analysis.

dye placed in the waste. Before dumping, the waste was dyed with 230 kg of a 20% solution of rhodamine WT. During initial samplings, the plume could be visually located, since rhodamine WT is bright red. A flow-through fluorometer was also used by James J. Bisagni (NOAA — Office of Marine Pollution Assessment) to track the waste plume in water pumped continuously from 3-m depth. The dye was used to track the transport and dispersion of the waste plume until neither dye nor waste could be measured.

SAMPLING

Surface water samples from a depth of 10 m were taken from the grid stations shown in Fig. 1. Samples were collected in organic-free 2-L ground-glass, stoppered bottles. They were obtained by lowering an empty 2-L bottle in a frame to the 10-m sampling depth. At that depth, the Teflon® stopper was pulled from the bottle by a line attached to the deck of the ship. After the bottle was filled, the sample was retrieved and stoppered immediately. All sampling bottles were precombusted at 500°C before use.

Prior to the dump on July 11, water samples were collected at station 21 (Fig. 1) on July 9 from depths of 10, 20, 50, 75, and 200 m. Samples at depth were collected with a General Oceanics Rosette sampler with 8-L Niskin bottles in conjunction with a Plessey 9040 STD. To avoid surface contamination, the STD−Rosette package was lowered to 500 m and the samples were collected as the Rosette was returned to the surface. Station 21 is near the center of the dumpsite and was used to monitor deeper waste levels prior to a dump. After the waste discharge on July 11, the waste plume, as identified by the rhodamine WT dye, was sampled at 2-m depth at 0.1, 0.5, 1, 2, 3, 4, 6, 9, and 12 h after dumping. At 4 h after dumping, samples from the waste plume were also collected with the STD−Rosette at depths of 10, 25, 50, and 75 m.

ANALYTICAL TECHNIQUES

The dynamic headspace method used to determine VOC in seawater is described by Sauer et al. (1978), Sauer (1978), and Atlas et al. (1980). The VOC were stripped from a heated (70°C) 2-L sample by an ultrapure helium stream at 135 mL·min^{-1} for 60 min and collected on Tenax-GC. One advantage of this stripping method is that the samples are not transferred before stripping, avoiding a possible source of contamination. The components trapped on the Tenax-GC were desorbed at 250°C for 10 min and retrapped on a liquid nitrogen cooled precolumn (see Fig. 3). When the desorbtion process was complete, the precolumn was switched into the chromatographic stream by a six-port valve. The trapped components on the precolumn were injected onto the chromatographic column by replacing the coolant with 90°C water. A 3.2-mm (outside diameter), 4.6-m stainless steel column packed with 10% SP-2100 on 80/100 mesh Supelcoport was used to separate and quantify the volatiles using a Hewlett-Packard 5830 gas chromatograph with a

TABLE 1. Percentages of TOC and volatiles in selected samples of ocean wastes dumped at DWD-106 during 1980.

	American Cyanamid barge effluent		DuPont Grasselli barge effluent		
Purge condition[a]	Apr. 2, 1980	Aug. 2, 1980	Mar. 11, 1980	Sept. 6, 1980	Nov. 7, 1980
TOC					
No purge	0.50	0.38	0.16	0.20	0.21
After 6-min purge	0.44	0.36	0.15	0.17	0.21
After 16-h purge	0.40	0.34	0.14	0.15	0.19
After 64-h purge	0.38	0.23	0.11	0.11	0.12
Volatile loss					
After 64-h purge (%)	24	39	28	45	43

[a]Purge rate was approximately 20 mL·min^{-1} through a 0.5% solution of waste in glass-distilled water.

flame ionization detector. During shipboard operation, the separating column was programmed at 50°C for 10 min, from 50 to 180°C at 4°·min^{-1}, and held at 180°C for 20 min. Standard procedures during shipboard analyses included blank sample analysis and frequent standardizations (standards added to prepurged seawater) using a mixture of aromatic and aliphatic hydrocarbons. While duplicate samples were not run during the shipboard experiment, due to time constraints (60-min purge and 60-min analysis), previous laboratory and shipboard duplicates indicate a 10% precision for this sampling and analytical technique. The component sensitivity of the method is <1 ng·L^{-1}.

For identification of volatile components by gas chromatography – mass spectrometry (GC/MS), the trapping and injection system (Fig. 3) was used to introduce samples into a Hewlett-Packard 5992 quadrapole gas chromatograph – mass spectrometer. The same column and operating conditions as previously described were used, except that the column oven was temperature programmed from 4 to 180°C at 4°·min^{-1} and then held at 180°C for the duration of the run. The lower initial temperature allows better separation of lighter volatile compounds. Mass spectra identifications were assisted by Heller and Milne (1978) and the NIH–EPA–MSDC Mass Spectral Search System and are reported following the GC/MS interpretation guidelines suggested by Christman (1982).

The VOC determined range in boiling point from near *n*-hexane (69°C) to *n*-tetradecane (254°C). Organic compounds outside this range are essentially unascertainable by this technique. However, some compounds with boiling points below that of *n*-hexane, such as acetone, can be qualitatively determined. The recovery of volatiles by the stripping technique depends on the type of organic compound. For hydrocarbons and halocarbons, the recovery is greater than 85% (Sauer et al. 1978). The more soluble ketones and alcohols have lower recoveries. Second purges were carried out on most samples to calculate the percentage of recovery for individual compounds.

Samples of five different barge effluents were also analyzed. For gas chromatographic determination of waste components, 25 μL of waste was added to 5 mL of prepurged seawater and analyzed with a Hewlett-Packard 7675A purge-and-trap system. The same chromatograph, column configuration, and shipboard temperature programming were used for component separation. The HP 7675A also traps on Tenax-GC but uses a small adsorbant mass and thus does not require the liquid nitrogen concentration before injection.

Total organic carbon (TOC) and percentage of volatiles were analyzed by the combustion technique of Fredericks and Sackett (1970). A 50-μL waste sample was added to 5 mL of distilled water in a break-seal combustion vial containing 0.25 mL of 10% phosphoric acid and 0.2 g of the oxidant persulfate. All samples were analyzed in triplicate. One set of samples (for TOC) was sealed immediately while others were purged with CO_2-free nitrogen for 6 min, 16 h, and 64 h before sealing and analysis. Although water evaporates during purging, the amount of nonvolatile organic carbon remains constant.

Results

TOTAL ORGANIC CARBON

Although the TOC concentrations and percentages of volatiles are somewhat variable (Table 1), the American Cyanamid waste contained about twice as much TOC as the DuPont samples we examined. TOC makes up less than 0.5% of the American Cyanamid waste and about 0.2% of the DuPont Grasselli waste. After 6 min of purging, between 9 and 12% of the American Cyanamid waste was removed, while 0 to 15% of the DuPont waste had been purged from the sample. After purging for 64 h, an average of 30% of the American Cyanamid TOC and 40% of the DuPont TOC was removed. Although the TOC of the waste was relatively low, the percentage of volatiles in the TOC was 30 to 40%, as determined by the 64-h purging. It should be noted that volatile percentages in the ocean-dumped TOC could be somewhat higher, since the wastes analyzed in our laboratory were shipped in bottles with large headspaces.

SPECIFIC WASTE COMPOUNDS

The component analysis by gas chromatography of the individual waste supports this contention. Only three or four compounds were observed in the waste supplied to us. The predominant compound in the American Cyanamid waste was toluene, comprising over 97% of all purgeable organics measured by gas chromatography. Several smaller peaks in the

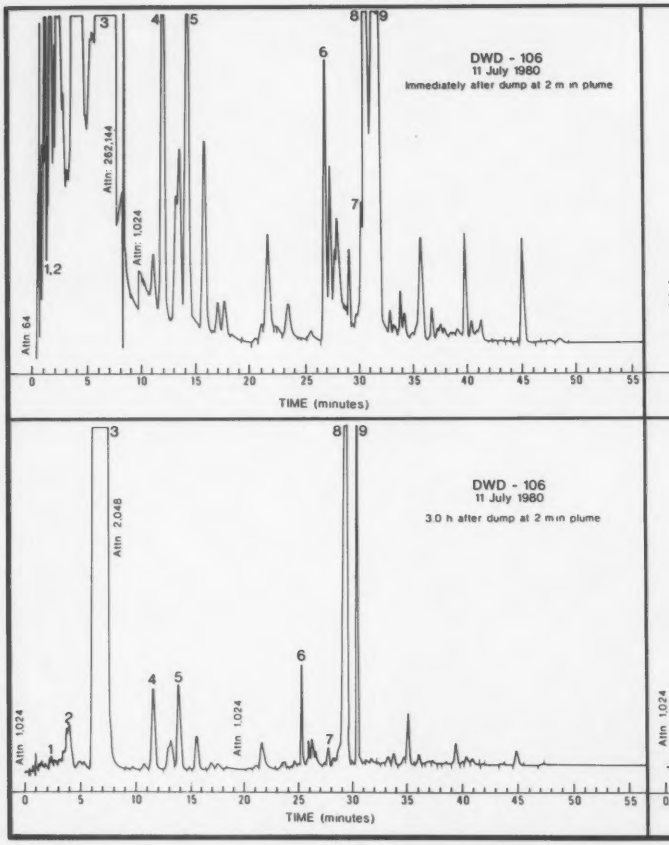

FIG. 4. Gas chromatograms showing relative distributions of VOC in the waste plume sur
Peaks 1 to 9, which were characteristic of the waste, are identified in Table 2. Waste conc

plume surface waters immediately after the dump and at 0.5, 3, and 6 h after waste discharge. aste concentrations for each chromatogram are shown in Table 3.

TABLE 2. Identification of major VOC in American Cyanamid waste dumped July 11, 1980, sampled in the water column immediately after dumping.

Peak	Compound	Identification confidence[a]	Molecular weight
1	Dichloroethane	2	98
2	C_6 aldehyde	1	98
3	Toluene	3	92
4	1,3-Dithiane	1	120
5	Bis-2-chloropropyl ether	1	156
6	Formaldehyde diethyl mercaptan	1	136
7	*O,O,S*-trimethyl dithiophosphate	1	172
8	Trichlorobenzene	3	180
9	Trichlorobenzene	3	180

[a]Confidence levels: 1, tentative structural assignment (electron ionization (EI) spectra match library spectra); 2, confident structural assignment (EI spectra supported by retention data); 3, confirmed structural assignment (EI spectra match both library and authentic standard spectra plus retention data support).

American Cyanamid waste chromatograms eluted earlier than the toluene and were not identified. Unfortunately, waste from the dump on July 11, 1980, was not made available for laboratory analysis prior to dumping. In contrast with the few peaks found in the laboratory sample waste chromatograms, the American Cyanamid waste analyzed from the barge plume after the July 11, 1980, dumping contained over 60 different compounds. Chromatograms of samples taken immediately after dumping and 0.5, 1, and 4 h after dumping are shown in Fig. 4. There are many small peaks indicating separate compounds and at least nine large peaks representing individual compounds (as identified by GC/MS) which we considered characteristic of the waste.

Mass spectra were obtained on 57 different organic compounds from the surface water sample (2 m) taken immediately after dumping. We did not try to identify all these chemicals. Rather, we concentrated on identification of the nine most abundant compounds in the dump (labeled 1 to 9 in Fig. 4). The compound identifications and molecular weights are given in Table 2. Dichloroethane (peak 1), toluene (peak 3), and two trichlorobenzenes (peaks 8 and 9) were at least confidently identified (see Table 2 for identification criteria), while several others (C_6 aldehyde, formaldehyde diethyl mercaptan, *O,O,S*-trimethyl dithiophosphate, bis-2-chloropropyl ether, and formaldehyde diethyl mercaptan) were given tentative structural assignments. We did not expect to find trichlorobenzenes in the waste, since none were found in our laboratory samples. The London Ocean Dumping Convention prohibits the ocean discharge of organohalogen compounds, such as trichlorobenzenes, except when present as trace contaminants or if they are rapidly rendered harmless by oceanic processes (Park and O'Connor 1981).

Visual observations of the waste plume indicated no surface slick, even though the sea surface conditions were calm and conducive to slick formation. Since slicks are formed by surface-active compounds, there must be few surfactants in the waste. None of the major VOC (Table 2) were highly surface active. Surfactant measurements made in the plume by dipping a germanium crystal into the surface water and analysis by internal reflectance infrared spectroscopy support the visual observations of little surface-active material in the waste (D. W. Goupil, Technology Feasibility, American Cyanamid Company, Stamford, CT 06904, personal communication).

WASTE DISPERSION AND BACKGROUND MEASUREMENTS

It was not the objective of our study to identify all the waste compounds but rather to track the dispersion of the waste by examination of the major components. For this time-series study, five compounds were examined (peaks 3, 4, 5, 8, and 9), representing toluene, two dichlorobenzenes, and two other compounds tentatively identified as 1,3-dithiane and bis-2-chloropropyl ether (see Table 2). As described previously, the waste plume was tracked continually, using rhodamine WT dye (both visually at first and later with a flow-through fluorometer) and two radar-reflecting drogued buoys, to ensure that the same water mass was sampled with time. During this time-series experiment, surface samples were not collected in the same geographic location. The plume was drifting to the north. At each time interval, samples were collected in the plume, as identified by the dye tracer and the drifter buoys. Water column analysis of the five designated waste compounds from surface water (2-m depth) samples collected from the plume immediately after dumping to 9 h after dumping indicates a relatively rapid loss or dilution of VOC from the surface waters during the first few hours after dumping (Table 3). The rapid loss of most compounds that elute before toluene on the chromatogram (probably light mercaptans), relative to the major peaks, indicates that initial loss of volatiles is due to evaporation (Fig. 4). This rapid evaporative loss was at least qualitatively confirmed by the strong odor of mercaptans observed when sampling the plume during the first hours after dumping, but absent later.

Comparison of gas chromatograms of VOC (Fig. 5) from a sample in the waste plume at 12 h after dumping and a background surface water sample, taken at station 29 2 d before the dump, indicates surface waters had returned to background levels by 12 h after dumping. The background concentration of toluene, the major VOC in the American Cyanamid waste, in the dumpsite area (Fig. 1) ranged between 5 and 40 $ng \cdot L^{-1}$ in the surface waters (10-m depth). However, one background sample taken near station 27 at the north end of the dumpsite had a toluene concentration of 220 $ng \cdot L^{-1}$. The thermocline depth from XBT data, indicating the depth of the surface mixed layer, varied during this period from 10 to 20 m. Samples collected before the dump using the STD−Rosette system at station 21 near the center of the dumpsite at depths of 10, 20, 60, 75, and 200 m also showed no appreciable waste at those depths, although the 10-m sample showed a total volatile level of 40 $ng \cdot L^{-1}$. About 50% of the VOC in the 60-m sample was benzene, which was not present in the waste, but which is a high percentage compound in natural, background volatile organic surface water samples (Sauer 1980). These data indicate no appreciable buildup of dumped material in the surface waters (down to 10 m) of the DWD-106 region from the previous dumps (see Fig. 2). All chromatograms taken prior to

TABLE 3. Time dispersion of dyed discharge waste from the tanker *Susan Frank*, July 11, 1980. Peaks 3 through 9 are characteristic of the waste.

Time (h after dump)	Dye (ppb)	Waste compounds ($\mu g \cdot L^{-1}$)[a]					Total VOC ($\mu g \cdot L^{-1}$)[b]
		3	4	5	8	9	
0.1	23.4	1750	19	20	110	45	2060
0.5	16.1	1170	21	21	120	44	1540
1	7.0	1010	51	20	69	43	1270
2	2.5	640	2.8	3.1	20	7.2	750
3	2.5	810	2.7	2.9	20	6.6	860
4	4.1	60	0.3	0.4	1.8	0.5	72
6	0.063	3.8	—	—	0.4	1.5	9
9	0.004	0.02	—	—	—	0.01	2

[a]Waste compounds 3, 4, 5, 8, and 9 are toluene, 1,3-dithiane, bis-2-chloropropyl ether, and trichlorobenzenes, respectively.
[b]Measured by gas chromatography.

dumping were relatively free of the peaks characteristic of the waste material (Table 3), except for the high toluene value at a single station.

A depth distribution was obtained at 4 h after the dump for comparison with the predump vertical profile. Samples were obtained at depths of 2, 10, 25, and 75 m. The 2-m sample was collected by bottle and line and the deeper samples were collected by STD−Rosette. The 10-m sample showed the same chromatographic pattern as the 2-m sample taken at the same time (Fig. 4), but the concentrations of both total waste and individual compounds were much lower. The toluene concentration at 10 m was only 0.01 $\mu g \cdot L^{-1}$ compared with 60 $\mu g \cdot L^{-1}$ measured in the 2-m sample. Samples taken at 25 and 75 m showed 0.05 and 0.03 $\mu g \cdot L^{-1}$ toluene, respectively. The predump levels of toluene at 20−200 m at station 21, approximately the same location as the 4-h postdump station, averaged 40 $ng \cdot L^{-1}$. The postdump depth distribution indicates slight transfer of waste toluene to deeper depths. Since the samples were taken from the bottom up, the STD−Rosette may have drifted out of the plume before the 10-m sample was taken. Csanady (1981) noted that since the waste is slightly more dense than seawater, it rapidly mixes throughout the well-mixed surface wastes. Thus, absence of waste in the 10-m sample must have resulted from missing the waste plume due to ship drift during the 30 min required to lower and raise the STD−Rosette sampler. Since all surface samples were taken in the plume by rapid hand lowering of the 2-L glass bottles, ship drift problems were avoided in the surface water collections but are a possibility in the vertical profile.

In summary, the results of this dump study showed that there was no appreciable buildup of waste in the dumpsite area prior to our study (except at one station) and that the waste was rapidly dispersed after dumping. By 12 h after dumping, it was difficult to ascertain that the plume was sampled (Fig. 5), except from the presence of the drogued buoys. At the 9-h sampling, however, the presence of dye and low levels of waste (2 $\mu g \cdot L^{-1}$) indicated that dilution by over 1000 times had occurred within 9 h. Although there is no other background toluene data available for this area, the 20 $ng \cdot L^{-1}$ of toluene observed at 9 h is about the same level as Sauer (1980) reported for aromatic concentrations in relatively clean surface waters of the Caribbean Sea. It should be noted here that the purge and trap technique measures only VOC within a certain analytical window. Fortunately, this window includes much of the waste dumped during our experiment. If some VOC are rapidly hydrolyzed or bacterially metabolized to nonvolatile organics after dumping, they will not be observed by this technique. Since the major VOC, including toluene and trichlorobenzene, are not rapidly hydrolyzed or metabolized in seawater, such processes probably have no major effect on components in our study.

Discussion

When an organic waste is dumped into the surface ocean, various processes begin to act immediately to reduce its concentration. These processes include evaporation, dissolution, dispersion, interactions with suspended particulate matter, photooxidation, and microbial degradation. Most of these processes act slowly, but some, especially evaporation and dispersion, can be rapid. By definition, VOC have a high vapor pressure and thus can easily evaporate. Unlike solid waste, VOC discharged into surface waters are lost to the atmosphere where they are rapidly diluted. The concentration of most VOC in marine air is below detection limits, except very near industrial or urban coastlines. Thus, the atmosphere is almost always a sink for volatiles in marine surface waters. Evaporation rates for VOC depend on both solubility and vapor pressure, but transfer velocities are often difficult to calculate. The initial removal-mixing process encountered by waste dumped in the ocean is simple mass dilution.

Csanady (1981) has discussed in detail the mixing processes associated with barge wastes dumped at DWD-106. He noted that initial dilution is accomplished by barge-bound eddies (wake dispersion) producing an initial dilution of up to a factor of 10 000. Subsequent dispersion by natural processes is lower, describable by an effective eddy diffusivity of 300 $cm^2 \cdot s^{-1}$. His calculations were based on waste dumped from a barge. Although the American Cyanamid waste studied here was pumped from a tanker, the wake dispersion effects should be similar.

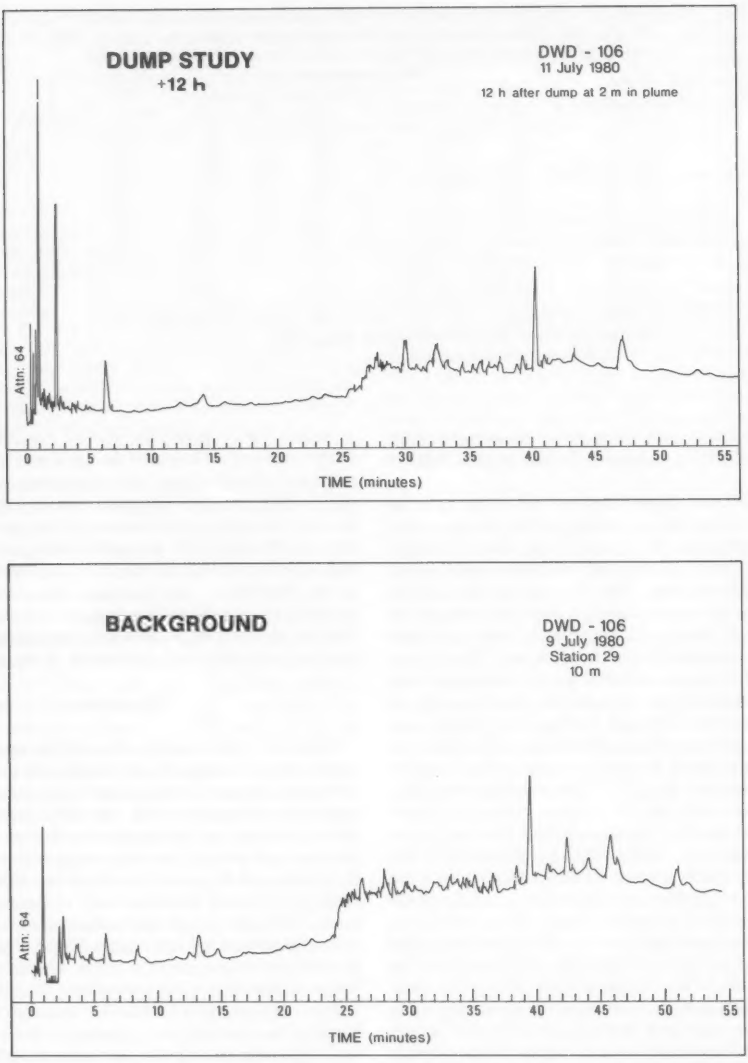

FIG. 5. Gas chromatograms of surface water organic compounds analyzed 12 h after dumping (top) and from a background station (see Fig. 1) sampled 2 d before the dump (bottom).

WAKE DISPERSION

The 1.4×10^6 L of waste dumped on July 11, 1980, was dyed with 230 kg of a 20% rhodamine WT solution. This translates into a dye concentration of 32 ppm, assuming the waste has a density of 1 $g \cdot cm^{-3}$. Csanady (1981) predicted an immediate initial dilution factor of up to 10^4. This wake dilution factor should reduce the initial dye concentration in our study to 3 ppb. The actual dye concentration that we measured in the sample collected immediately after dumping was 23 ppb (Table 3). This value represents an initial dilution factor of about 10^3, or more accurately a dilution of 1300.

The initial dye dilution in this study agrees within an order of magnitude with the maximum value calculated by Csanady (1981) for wake dispersion. The lower value may be explained possibly by the fact that the waste on July 11, 1980,

was pumped from a tanker and not from a barge. Instead of forming a long column of waste, the dyed waste appeared to initially form patches separated by several to tens of metres. Wake dispersion may have been lower in these patches. Nonuniformity of dye distribution throughout the waste could account for the higher dye values observed at 4 h after the dump (Table 3) when dye concentrations increased to 4.1 from 2.5 ppb at 3 h postdump, while the toluene values decreased. While we cannot rule out this possibility, the general concurrent decrease in VOC and dye (Table 3) indicates that inhomogeneity of dye and waste was not significant.

If we assume that the waste was uniformly dyed, the initial waste concentration after dumping can be calculated. Total organic carbon makes up about 0.5% of the American Cyanamid waste, and roughly half of the TOC is VOC, mainly toluene. This value for volatile percentages is higher than in Table 1, but a higher value accounts for losses of mercaptans and other volatiles during TOC sample shipment. Thus, 2.5 g VOC·kg waste^{-1} is found in the dumped material. From the initial dye concentration, we know that the wake dispersion reduces the waste concentration by a factor of 1300. This dilution would predict an initial surface water waste concentration of 1900 ppb, or assuming a water density of 1 kg·L^{-1}, 1900 μg·L^{-1}. This predicted value is approximately the same as the 2060 μg·L^{-1} that we measured in the 0.1-h waste discharged sample (see Table 3). Thus, with the dilution factor calculated from the dye in the plume, the initial wake dispersion of the waste can be predicted.

Natural Dispersion Processes

The patches formed by the waste discharge, in lieu of a single waste stream, complicated the comparative sampling with time after the discharge. Great efforts were made to determine that the same waste patch was tracked and resampled at each of the time intervals (up to 9 h) shown in Table 3. In this experiment the dye concentrations decreased with time for the first 2 h with the same trend as had been observed for previous dye studies at DWD-106 (Csanady 1981). At 3 and 4 h after dumping, however, the dye concentrations fell above the predicted mixing curve. Such data scatter in dye studies is not uncommon and probably results from some initial nonhomogeneous mixing in the surface waters. Initial distributions of VOC in the waste are probably somewhat variable also. Toluene levels increased in the waste plume by 20% (twice the analytical error) between 2 and 3 h, while the dye level remained constant. Subsequently, the dye concentration in the waste increased between 3 and 4 h (Table 3), while the toluene levels and those of other characteristic volatiles decreased. While the time-series trend was clear, the possible inhomogeneity of the waste–dye mixing process made it impossible to use the dye as a conservative indicator of mixing to calculate VOC evaporation rates, as had been done in previous studies (Schwab et al. 1981; Brooks et al. 1983).

While the dye dispersion results showed some variability, the loss of VOC from the 2-m samples was both obvious and rapid. A comparison of the waste chromatogram from 0.1 h with the sample taken at 0.5 h after dumping (Fig. 4) shows that most of the compounds before toluene (peak 3) have been lost from the surface waters. The strong mercaptan smell observed on deck during the initial sampling indicated that many light sulfur compounds were being rapidly lost from the waste. Apparently, the American Cyanamid waste has high initial concentrations of mercaptans, although only one (peak 6) was specifically identified by GC/MS on the stored samples. This was not surprising, since mercaptans do not store well and are difficult to analyze. When the American Cyanamid waste is loaded onto the barge *Sparkling Waters*, only two of the eight compartments can be used, since only two compartments have hatches to contain the mercaptans. The gas-tight compartments prevent the mercaptans from wafting over the New Jersey coastline setting off gas alarms in the area (T. P. O'Connor, NOAA, Rockville, MD 20852, personal communication). A comparison of the 0.1- and 0.5-h chromatograms, along with the olfactory analysis of surface air after the initial dumping, indicated that these mercaptans are rapidly evaporated from the waste in the surface waters.

Evaporation of Volatiles

Our observation of no discernable waste buildup in the dumpsite just prior to the July 11, 1980, dump was not consistent with an earlier background study (T. P. O'Connor, NOAA, Rockville, MD 20852, personal communication) which indicated a noticeable buildup of VOC in the surface waters between dumps. Between November 14 and 16, 1980, Dr George Harvey of NOAA/AOML measured volatile organics in surface water bucket samples at DWD-106. The previous dump of organic waste was on November 11. During this survey, one high value of 4090 ng·L^{-1} was observed near the center of the dumpsite, with the rest of the background stations averaging 158 ng·L^{-1} (SD = 201 ng·L^{-1}, n = 45). Four samples had concentrations over 300 ng·L^{-1}. These high values, equal to levels in the Mississippi River plume (Sauer 1978), indicate a buildup of waste from previous dumps, although many zero values were observed in the southeast quadrant. In our study, however, VOC concentrations in the background stations were low, and levels in the dump site returned to predump values within 12 h after dumping. Zooplankton samples were also taken before the dump and analyzed by Energy Resources Co., Inc. for nonvolatile or semivolatile organic compounds characteristic of the waste (Boehm 1981). This sampling was conducted to search for bioaccumulation of waste products from previous dumps. Boehm (1981) noted that background levels of organics characteristic of the waste in the zooplankton were generally nondetectable to very low, as we had also observed for the VOC in the water samples. Only one zooplankton sample contained compounds (methylcyclopentanonediene and cyclohexanone) also found in the waste. Subsequent to dumping, waste-associated compounds were detected in the samples for up to 23 h.

Taken together, these results indicate that the dispersion processes during this study at DWD-106 were of sufficient magnitude to rapidly reduce wastes to background levels. However, the low levels may be due in part to the nature of the waste dumped during the study and to increased water movement and mixing since the last waste was dumped (Fig. 2). The organic fraction of the American Cyanamid

waste was very volatile. As stated earlier, there were some mercaptans in the waste (as determined by smell), and most of these were lost in the initial 30 min after dumping. The main component of the waste was toluene (>85% VOC), which is only slightly soluble in seawater (approximately 400 $mg \cdot L^{-1}$) (Rossi and Thomas 1981) and should volatilize rapidly in the presence of wind waves (Cohen et al. 1978). High volatilization rates for compounds in the waste would rapidly lower their concentration and also produce the rapid losses that were observed. If the same type of compounds were dumped during the previous dumping on July 4 and 6, 1980, then this could account for the low background values. Schwarzenbach et al. (1978) calculated that all volatiles could diffuse from a 3-m water column within 4 days, and Csanady (1981) suggested that this time was sufficient to disperse the dye to undetectable levels.

The transfer of VOC from the ocean to the atmosphere can be conveniently estimated using the stagnant film model of Kanwisher (1963) and Broecker and Peng (1974) to calculate the flux of a compound between the water and air phases, assuming that the concentrations on either side of the stagnant boundary layer are in equilibrium, as can be expressed by a Henry's law constant. Analysis using a two-layer model is also possible (Sauer 1978), but it is often difficult to estimate the liquid and vapor phase mass transfer coefficients under natural conditions (Cohen et al. 1978). The stagnant film model predicts the flux (F) in terms of the molecular diffusivity (D) of the compound and the thickness of the stagnant diffusion-controlled boundary layer, z:

$$(1) \quad F = -D(dc/dz)$$

where dc is the concentration difference across the film layer. If we assume that the air concentration is zero, then dc is the surface water concentration. Assuming a film thickness of 65 μm, corresponding to a mean windspeed of 6.3 $dm \cdot s^{-1}$, and using a molecular diffusivity of 10^{-5} $cm^2 \cdot s^{-1}$, one can calculate a toluene flux (dc = 1750 $\mu g \cdot L^{-1}$) of 3×10^{-5} $g \cdot m^{-2} \cdot s^{-1}$.

The residence time (τ) in the surface water mixed layer (10 m in this case) can be calculated from the initial toluene concentration (c) and the evasion rate of toluene from the ocean as calculated in Eq. 1:

$$(2) \quad \tau_{exchange} = c/(dc/dt)$$

$$= \frac{(1.8 \times 10^{-6}\ g \cdot cm^{-3})\ (10 \times 10^{6}\ cm^3 \cdot m^{-2})}{3 \times 10^{-5}\ g \cdot m^{-2} \cdot s^{-1}}$$

$$= 6.0 \times 10^5 \text{ s or } 6.9 \text{ d.}$$

It is obvious from the postdump data for toluene (Table 3) that the residence time is much less than 6.9 d. If this residence time for toluene was representative for other dumpings at DWD-106, a large background level of toluene from previous dumps (Fig. 2) should be observed in the dumpsite area. Since this was not the case, venting of VOC to the atmosphere cannot alone account for the loss of these compounds from the dumpsite area. Other dispersion processes must be responsible. One process could be higher eddy diffusivities than predicted by Csanady (1981) due to the passage of a warm-core eddy through the dumpsite.

Eddy-Enhanced Dispersion

The physical mixing regime of the DWD-106 surface waters is strongly affected by Gulf Stream warm-core eddies which regularly traverse the dumpsite area. Four different eddies passed through the dumpsite during 1979. The edge of an extremely large warm-core ring was in the dumpsite area during our sampling cruise in July 1980. This eddy (designated 79-H by the NOAA Atlantic Environmental Group) formed from the Gulf Stream on September 18, 1979. In May 1980, this large anticyclonic ring had a surface diameter of 179 km as it crossed west of 70°N latitude into the slope waters south of New England. Figure 6 shows two surface temperature analysis maps made by NOAA using the NOAA-6 satellite advanced very high-resolution radiometer (AVHRR). These analyses were made on July 9 and 16, 1980. The anticyclonic water circulation of the warm eddy (WE) near the dumpsite is shown by the arrows.

During our sampling cruise, the Gulf Stream water encircling the warm Sargasso Sea water in eddy 79-H was moving through the dumpsite area (Fig. 6). The exact location of the eddy during the dump was verified by analyzing high-resolution AVHRR data from a satellite pass over the dumpsite area made at 23:23 GMT on July 11, 1980. The dump began at 18:30 GMT. The AVHRR data (Fig. 7) clearly show that the edge of the eddy bisected the dumpsite on a line from the southwest to northeast corner (see Fig. 1). The dump on July 11, 1980, was made in the southeast quadrant of the dumpsite in the shear boundary of the eddy. The division of the dumpsite by the ring was verified by the XBT temperature profiles obtained during the cruise. The anticyclonic eddy transport was moving the water from the northeast to the southeast in the dumpsite region.

This was the general direction of the plume drift during our experiment. The effect of this water mass transport would be twofold. The transport of relatively clean Gulf Stream water through the dumpsite could displace water from previous dumps, since eddies tend to have cycle times of less than a week. This displacement of polluted water would account for the low levels of VOC observed in the samplings before the dump, both in the water and in the zooplankton samples. After dumping, the eddy diffusivity in the dumpsite would be high due to the surface currents associated with the warm eddy.

Flierl and Dewar (1983) have modelled the motion and spreading of waste under the influence of a strong eddy. They predict rapid northward motion (for an anticyclonic eddy), with the plume becoming very elongated as it passes through the region where the current velocity is strongly increased. This leads to enlarged gradients and increased diffusion of material into fluid which would normally be further away. Thus, the ring causes an enhancement of the dispersion which would normally occur due to the smaller scale motions. During our study, ring 79-H was at the edge of the dump area. Current velocities at ring boundaries, which increase mixing, are higher than at the center (Olson 1980), often reaching current velocities of 1.6 $m \cdot s^{-1}$ (probably somewhat lower in this older eddy). The phenomena we observed during this

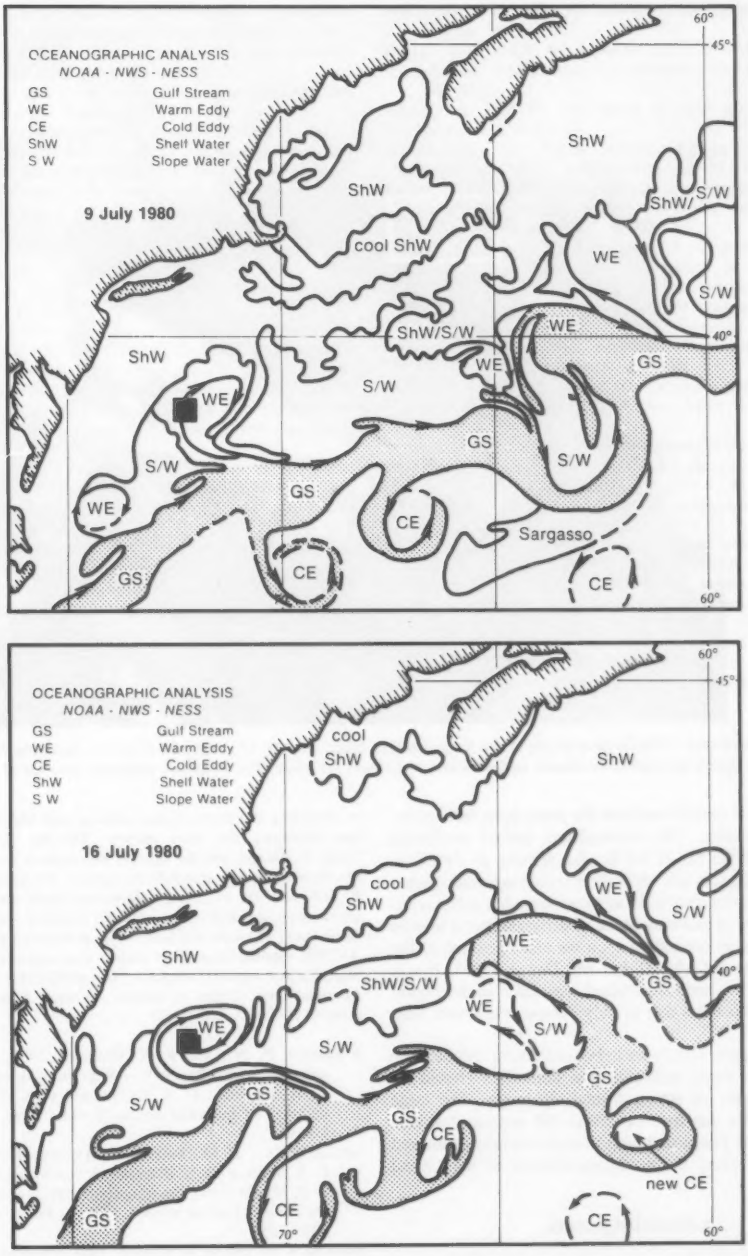

FIG. 6. Oceanographic analysis of surface water temperature compiled from the NOAA-6 satellite AVHRR on July 9 and 16, 1980. The dumpsite is noted as a black square, and the stippled area indicates the location of the Gulf Stream.

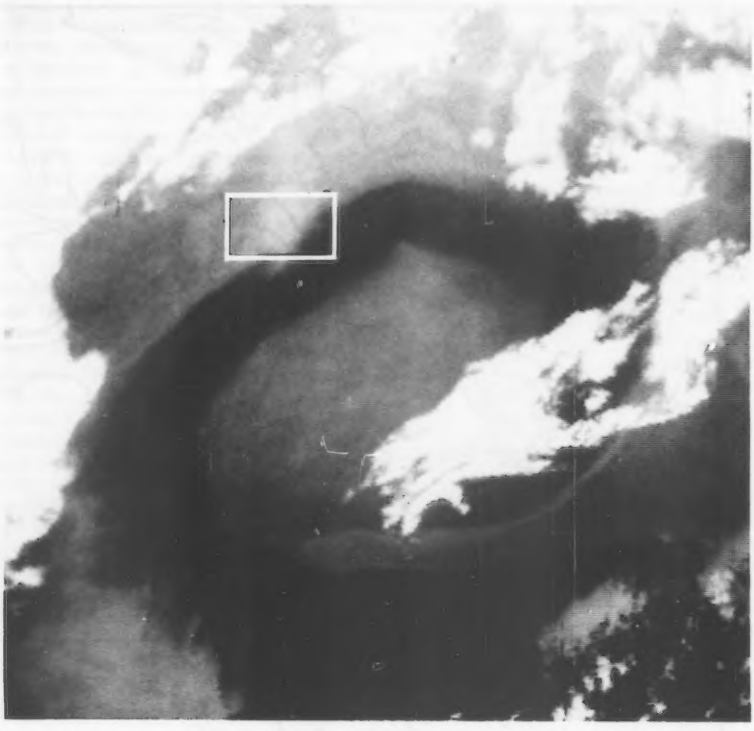

FIG. 7. High-resolution AVHRR photograph of the dumpsite area taken on July 11, 1980, 23:23 GMT, from the NOAA-6 satellite (orbit 5406). The darker area indicates warmer surface water, and clouds are white. The white box marks the location of DWD-106.

dump experiment closely matched the predictions from eddy-enhanced dispersion. The waste-plume drifted northward beginning at 38°45′N, 72°10′W and drifting to 38°50′N, 72°14′W. Mixing was also several orders of magnitude higher than would be predicted without increased eddy diffusivity. The exact direction and magnitude of eddy-enhanced motion are very sensitively dependent upon the exact position of the dump relative to the eddy (Flierl and Dewar 1983). It was fortuitous that the dump we studied was made in the region where mixing processes due to eddy–waste interaction were most enhanced.

If volatile organic wastes are to be continually dumped into the ocean, this study indicates that dumpsites should be located in regions of strong frontal dynamics. The large number of eddies that traverse DWD-106 suggest that it is more suitable for ocean dumping than are dumpsites located closer to shore along the northeastern coast of the United States.

Acknowledgments

We thank Je-Kwon Kim and Zubir Din for their tireless assistance in the sampling and shipboard analyses during the *Mt. Mitchell* cruise. We also acknowledge the assistance of Hessein Abdel-Reheim in analyzing the total organic carbons and Mahlon C. Kennicutt for identifying the mass spectra. The aid of Chief Scientist James J. Bisagni and the officers and seamen of the NOAA ship *Mt. Mitchell* are also gratefully recognized. We acknowledge Thomas P. O'Connor for supplying information about the dumped waste, previous unpublished studies, and his technical comments. We also thank Paul LaViolette and Ron Holyer of NORDA for processing our AVHRR satellite data. This project was supported by the United States Department of Commerce, National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment, through contract NA80AA-D-00036.

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Coupling of Organic Pollutants Between the Estuary and Continental Shelf and the Sediments and Water Column in the New York Bight Region[1]

PAUL D. BOEHM[2]

Environmental Sciences Division, ERCO (Energy Resources Co. Inc.), One Alewife Place, Cambridge, MA 02140, USA

BOEHM, P. D. 1983. Coupling of particulate organic pollutants between the estuary and continental shelf and the sediments and water column in the New York Bight region. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 262–276.

The composition and distribution of polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and coprostanol in suspended particulate matter in the Hudson River – Lower Bay – New York Bight system were investigated. Fused silica capillary gas chromatography and gas chromatographic mass spectrometry were employed for PAH, PCB, and coprostanol determinations. Additionally, dredged material and sewage sludge waste deposits from the bight were size fractionated and analyzed. Between the estuary and shelf and between the benthos and water column, chemical flux mechanisms included Hudson River sediment resuspension and bottom water transport within the estuary, sewage effluent input to harbor–river surface waters followed by seaward transport, landward transport of resuspended bight sediment linked to resuspension of PAH-rich dredged material, and possible transport of sewage-associated organics down the Hudson Valley. The composition of PAH and PCB varied with sediment grain size. Dredged materials were rich in pyrogenic PAH, while PAH in sewage sludge were mainly of a petroleum origin. PAH, PCB, and coprostanol levels were decoupled in the water column particles, probably due to differential solubility behavior of the three compound classes.

BOEHM, P. D. 1983. Coupling of particulate organic pollutants between the estuary and continental shelf and the sediments and water column in the New York Bight region. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 262–276.

Nous avons étudié la composition et la distribution des hydrocarbures aromatiques polynucléaires (HAP), des diphényles polychlorés (PCB) et du coprostanol dans la matière particulaire en suspension dans le réseau fleuve Hudson – baie inférieure – baie de New York. La chromatographie en phase gazeuse sur capillaire en silice fondue et la spectrométrie de masse chromatographique gazeuse ont été utilisées dans la détermination de ces trois substances. En outre, les déblais de dragues et les dépôts de boues d'égouts dans la baie de New York ont été fractionnés par taille et analysés. Parmi les mécanismes de flux chimique entre l'estuaire et le plateau, et entre le benthos et la colonne d'eau, on note la resuspension des sédiments du fleuve Hudson et le transport des eaux du fond dans l'estuaire; les apports d'égouts dans le port–eaux de surface du fleuve, suivis d'un transport vers la mer; le transport vers la terre des sédiments resuspendus de la baie, lié à la resuspension des déblais de dragues riches en HAP; et le transport possible, dans la vallée de l'Hudson, de matière organique associée aux eaux usées. La composition des HAP et PCB varie en fonction de la taille des grains du sédiment. Les déblais de dragues sont riches en HAP pyrogéniques, tandis que les HAP des boues d'égouts sont en grande partie d'origine pétrolière. Les HAP, PCB et le coprostanol sont séparés dans les particules de la colonne d'eau, probablement par suite de différences de solubilité de ces trois substances.

Received March 19, 1982
Accepted October 4, 1982

Reçu le 19 mars 1982
Accepté le 4 octobre 1982

MAJOR coastal population centers substantially influence the chemistry of adjacent marine waters and sediments by virtue of pollutant fluxes into the system. The mechanisms of pollutant introduction are numerous. In the estuarine and continental shelf system of the Hudson and Raritan rivers and New York Bight (Fig. 1) the inputs can be broadly defined as continuous (i.e. riverine inputs of varying flow rates) and intermittent (i.e. ocean dumping events). Riverine inputs,

[1]This article forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Battelle New England Marine Research Laboratory, 397 Washington Street, Duxbury, MA 02332, USA.

Printed in Canada (J6868)
Imprimé au Canada (J6868)

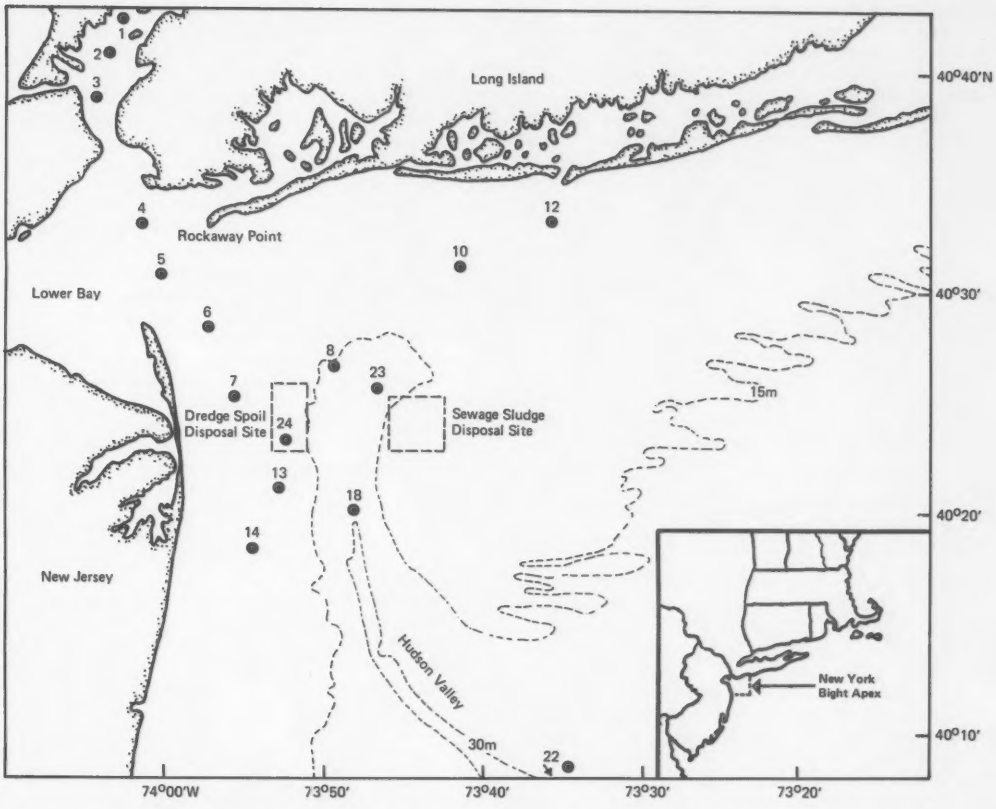

FIG. 1. Location of sampling stations in the New York Bight apex, mouth of the estuary (4, 5), and New York Harbor (1, 2, 3).

which couple to the shelf system through fluxes of pollutants through the Hudson River Estuary, actually consist of a myriad of point sources including sewage treatment plant effluents, resuspended contaminated sediments, stormwater runoff, and inputs from shipping activities (Atwood et al. 1979; O'Conner and Stanford 1979). Ocean dumping in the New York Bight results in the input of organic pollutants mainly from the disposal of contaminated dredged materials from the outer and inner harbors and sewage sludges from various treatment plants in the metropolitan New York area.

Of the host of organic compounds introduced into the system through both riverine fluxes and ocean dumping events, the polynuclear aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) compound classes are of primary concern because of their well-documented toxic and carcinogenic properties. These classes along with the chlorinated pesticides are considered "major perceived threats" to the "health" of the environment (O'Conner and Stanford 1979) and have been the focus of numerous investigations in recent years concerning ambient levels in bight sediments (West and Hatcher 1980; Boehm 1980a; Laflamme and Hites 1978; Farrington and Tripp 1977; MacLeod et al. 1981), levels in sediments and suspended matter in the Hudson River (Bopp et al. 1981), levels in the Raritan Bay sediments and biota (Stainken and Rollwagen 1979), and levels in biota from the bight (Boehm 1980b; MacLeod et al. 1981; O'Connor et al. 1982). These compound classes are important toxicologically, but their potential use as powerful source tracers when used in conjunction with one another and with the resistant sewage indicator sterol, coprostanol (Hatcher and McGillivary 1979; Walker et al. 1982), has not been adequately explored.

Several recent studies have addressed the short-term chemical perturbations in the water column during and immediately after disposal of sewage sludge (Hatcher et al. 1978) and dredged material (Boehm and Fiest 1983). During dumping events, physical and chemical fractionation of the dumped materials profoundly affect the dissolved and particulate fraction chemistries of seawater. The dissolved plume remains above the thermocline (Hatcher et al. 1978) where it becomes

diluted through mixing and advection. The bulk of particulate plumes rapidly penetrate the thermoclines and sink (Hatcher et al. 1978; Boehm and Fiest 1983), but residual particles remain detectable through PCB, PAH, and coprostanol measurements after 6 h.

Although some information exists on the effects of dumping on the water column's organic chemistry, virtually no information pertaining to estuarine–shelf and benthic–water column fluxes of these important pollutants exists. This research was designed to fill those informational gaps and address the following questions: (1) What are the levels and detailed chemical nature of PAH and PCB compounds in suspended matter in the estuary? (2) What are the levels, areal distributions, and detailed chemical nature of PAH and PCB compounds in New York Bight surface, intermediate, and bottom waters? (3) What is the relative importance of the waste deposits (spoils and sludge) as sources of PCB and PAH to the overlying waters through resuspension vis-a-vis estuarine–shelf fluxes of PAH and PCB bearing particulates (i.e. in nondump situations)? (4) Can a combination of parameter measurements on organic pollutants relate environmental chemical distributions to source material?

Methods

Sampling

The main sampling plan on R/V *Kelez* cruise RP-28-KE-80 (August 9–25, 1980) was to obtain suspended particulate samples from the water column of the Hudson–Raritan Estuary (stations 1, 2, 3, Fig. 1), from a tidal time series at the entrance to the estuary (station 4), from stations in the proximity of the sewage sludge and dredged material disposal sites (stations 23 and 24, respectively), from several stations between the dumpsites and the mouth of the estuary (stations 5, 6, 7), from the head of the Hudson Canyon or Valley (station 18), and along the New Jersey (stations 13, 14) and Long Island (stations 10 and 12) shorelines. Samples of the waste deposits were obtained from the dredged material and sewage sludge sites.

To obtain the suspended particles an all-Teflon underway-towed pumping system (UTPS) was used to pump water through a specially designed stainless steel filtration manifold located in the ship's wet laboratory. In-line precombusted (450°C) glass fiber (Gelman A/E, 142-mm diameter) filters were used to filter between 20 and 60 L of seawater. The pumping rate through the filter was 3–4 L/min. Samples were taken from surface water and intermediate or near bottom locations at each station for organic constituent studies. Separate samples were processed by scientists from the University of Rhode Island for total suspended matter (TSM) measurements. Sediment samples were taken using a Smith–MacIntyre grab sampler or alternatively by divers. Diver-obtained cores from the dredged material disposal site (station 24) were approximately 1 m long. All samples (filters and sediments) were stored and shipped in noncontaminating containers frozen at −20°C.

Analytical Methods

Processing of filters (suspended particles) — As all samples were to be used for PCB, PAH, and steroid determinations, a single processing scheme was utilized to maximize the usefulness of a very small amount of extracted material. The method of choice involved organic solvent extraction and alumina – silicic acid fractionation (column chromatography) into three fractions: f_1 (saturated hydrocarbons), f_2 (PAH and PCB), and f_3 (steroids).

Extraction was performed using the method of ambient temperature shaking (Brown et al. 1980; Boehm et al. 1981) wherein the filter is thawed, cut into strips, and introduced into a screw-top Teflon jar (250 mL). Distilled methanol is added first to dry the filter. The filter–solvent mixture is shaken for 4 h; the methanol–water mixture is decanted and replaced with an azeotropic mixture of methylene chloride and methanol (9:1). Internal quantification standards are added at this point (deuterated phenanthrene, androstane). Extraction–shaking continues for an additional 16 h at which time the extracts are combined in a separatory funnel, distilled water is added to the extracts, and the organic (methylene chloride) phase is obtained. The methylene chloride is concentrated, displaced with hexane, and fractionated using alumina – silicic acid adsorption column chromatography.

Processing of sediments — Sewage sludge and dredged material core fractions (a 0- to 4.5-cm sand layer and a 4.5- to 9-cm mud layer) were wet sieved (distilled water washing) through 1-mm, 250-μm, and 66-μm mesh sizes. Material coarser than 1 mm was discarded. The sand fraction consisted of a combination of material trapped in the 250- and 66-μm sieve. Silt and clay were separated from each other through a combination of settling (silt) and centrifugation and flocculation (NaCl + HCl). The particle size of the clay was assumed to be <5 μm (Thompson and Eglinton 1978). Each size fraction was weighed, a small subsample was taken to determine dry weight, and the fractions were extracted separately, using the ambient temperature shaking procedure as for the filters. The sediment washings were analyzed separately and yielded no detectable quantities of the compounds of interest.

Fractionation and analysis — Saturated hydrocarbon (f_1), aromatic hydrocarbon and PCB (f_2), and polar (f_3) fractions are obtained through elution of the column (1 cm inside diameter) of 1 g of 5% deactivated alumina and 10 g of fully activated silica gel (80–100 mesh) with 17 mL of hexane (f_1), 21 mL of hexane – methylene chloride (50:50) (f_2), and 25 mL of methanol (f_3), respectively. PAH from two to five rings were analyzed directly by fused silica glass capillary gas chromatographic mass spectrometry (GC^2/MS) using a Hewlett-Packard model 5985 GC/MS–computer system. A 30-m SE-52 fused silica capillary column (0.25 mm inside diameter) was used in both GC^2/FID (capillary gas chromatography with flame ionization detection) and GC^2/MS analyses. Analytical conditions for GC^2/MS were as follows. Temperature program: 40–290°C at 3°C/min; carrier flow: helium at 1 cm/3 min; injection port: splitless, all glass, 250°C; detection: mass spectrometer; ionization voltage: 2200 eV; scan rate: 40–400 amu, 1 scan every 1.5 s. Parent ion (m^+) total ion currents were computer-integrated, and areas were related to the area of the parent ion of the internal

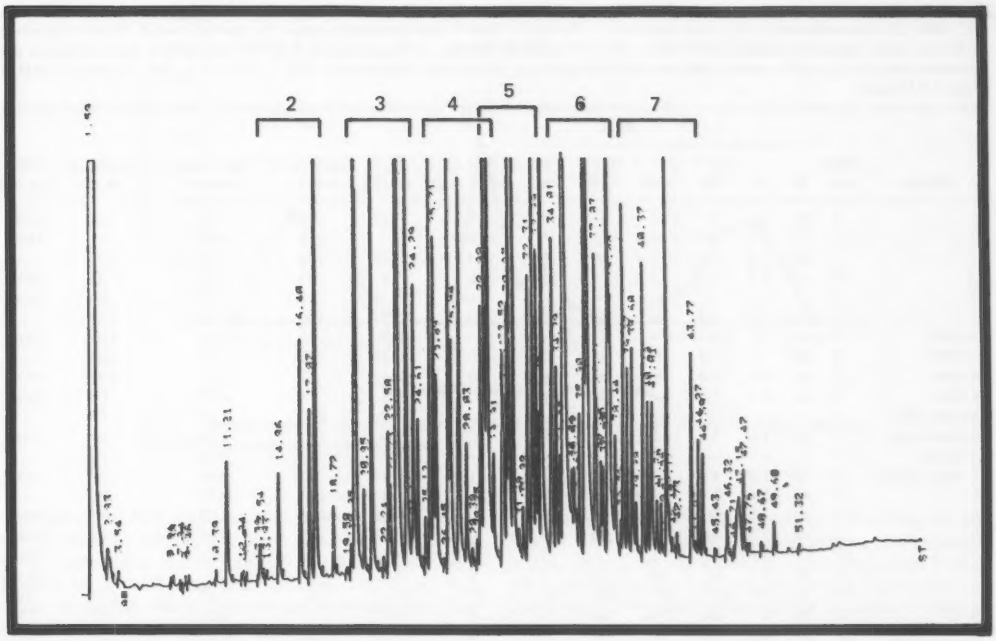

FIG. 2. Fused silica capillary gas chromatographic trace of mixed Aroclor (1016, 1242, 1254, 1248) standard (numbers refer to number of chlorine atoms).

standard. Relative response factors were computed using quantitative standard mixtures, and these factors were incorporated into the quantification program. Quantification of aromatic hydrocarbons by GC^2/MS agrees with that obtained by GC^2/FID to within 20%.

The f_2 fractions were also analyzed by GC^2/ECD (electron capture detector) (see Ballschmiter and Zell 1980) for PCB determinations. A mixed Aroclor standard (Fig. 2) was analyzed by GC^2/MS to determine the number of chlorine substitutions on each resolved component. Subsequently, the retention times of these identified compounds were compared with those of each eluting sample peak, definitive PCB isomeric family identifications were made (Cl_2 to Cl_7), and areas of each isomeric family were summed and quantified relative to an external standard dilution curve of selected Cl_2 to Cl_7 isomers. Reponse factors were determined for each family for at least two individual compounds and averaged to arrive at a single factor for each isomeric family.

The f_3 (polar) fractions were analyzed for coprostanol and other sterol components using the method of Hatcher and McGillivary (1979). This method involves the silylation of the dried f_3 eluate using *N,O*-bis(trimethylsilyl)acetamide in pyridine solution to form the trimethyl (TMS) ethers of the sterol compounds. The TMS ethers are then analyzed by GC^2/FID and quantified relative to an external standard (cholestane) spiked to the injection solution prior to analysis. The identities of the TMS ethers were confirmed by injecting silyated standard sterols onto the 30-m SE-30 fused silica column and by periodic sample coinjection. (Note that coprostanol and one other unidentified sterol coelute on SE-52 columns.)

Results

WATER COLUMN PARTICLES

Absolute levels of PAH in the estuary, bight — Concentrations of PAH compounds in the suspended particles ranged from nondetectable (<0.5 ng/L = parts per trillion) to 370 ng/L in the study region including the lower Hudson River and New York Bay through the mouth of the estuary and out to the shelf break (station 22) (Table 1). The mean total PAH concentration within the estuary (landward of Rockaway Pt.) was 13 ng/L (range nondetectable to 35 ng/L). PAH concentrations decreased and remained low during the ebb tide at station 4 (1−3 ng/L). Except in two cases, PAH concentrations in the bight were between <0.5 and 18 ng/L. In the bottom waters at stations 10 and 7, the PAH levels were elevated by an order of magnitude to 370 and 110 ng/L, respectively. Station 7 is located adjacent to the dredged material disposal site and this could account for the elevated PAH concentrations found there. However, station 10 is located at some distance from both the dredged material and sewage sludge disposal sites so the elevated PAH

TABLE 1. Concentrations of particulate organic pollutants in the water column. N = *m/e* 128, 142, 156, 170 (naphthalenes); P = *m/e* 178, 192, 206, 220 (phenanthrenes); nd = none detected = <0.5 ng/L; TSM = total suspended matter (D. Mukherji and R. Kester, University of Rhode Island, unpublished data); *m/e* = 202, 228, 252 represent amounts of fluoranthene and pyrene (tetracyclic), benzanthracene and chrysene (tetracyclic), and benzofluoranthrenes and benzopyrenes (pentacyclic), respectively; (228 + 252)/(P + 202) = group II PAH to group I PAH ratio.

		ng/L												
Station	Depth (m)	N	P	*m/e* = 202	*m/e* = 228	*m/e* = 252	Total PAH	(228 + 252)/ (P + 202)	PCB (ng/L)	Coprostanol (ng/L)	Coprostanol/ steroids	Coprostanol/ PCB	TSM (μg/kg)
1	3	nd	2	4	1	—	7	0.2	0.24	66	0.25	280	2400
1	8	0.3	3.4	6.3	3.0	3.1	16	0.6	2.2	56	0.08	25	1800
2	3	nd	1.4	6.4	3.8	4.7	16	1.1	0.44	170	0.24	380	—
2	8	nd	8.7	11.7	7.8	7.6	35	0.8	1.4	27	0.18	20	2500
3	3	—	—	—	—	—	—	—	0.32	18	0.26	56	2800
3	3	0.5	0.6	1.5	nd	nd	2.6	0	0.93	100	0.22	120	—
4 (ebb)	5	—	—	—	—	—	—	—	0.50	56	0.15	110	2300
4 (ebb)	3	nd	1.0	1.5	nd	nd	2.5	0	0.43	76	0.11	180	—
4 (ebb)	3	nd	0.4	0.5	nd	nd	0.9	0	0.49	79	0.11	160	2400
4 (ebb)	5	nd	0.8	1.4	nd	nd	2.2	0	2.8	43	0.17	15	2000
4 (low ebb)	5	—	—	—	—	—	—	—	3.0	230	0.24	77	—
4 (slack ebb)	5	nd	1.0	3.2	1.5	2.3	8	0.9	3.5	130	0.18	36	880
4 (flood)	5	—	—	—	—	—	—	—	1.2	93	0.36	78	—
4 (high flood)	3	nd	1.5	4.3	3.6	3.4	13	1.2	0.49	47	0.06	96	1200
5	3	nd	3.4	3.4	4.0	8.5	19	1.8	1.8	160	0.13	88	—
5	14	nd	1.0	2.1	nd	nd	3.1	0	0.12	6	0.02	50	2900
6	3	nd	0.5	nd	nd	nd	0.5	0	0.11	5	0.05	45	3000
6	12	3.5	4.8	4.4	2.2	2.3	17	0.5	0.22	—	—	—	2000
7	3	nd	6.7	nd	nd	nd	7	0	0.16	—	—	—	1600
7	10	nd	nd	21	150	200	370	13	0.67	83	0.15	120	500
8	15	nd	1.1	nd	nd	nd	1	0	0.11	11	0.04	100	350
8	25	nd	0.8	0.9	nd	nd	2	0	0.10	12	0.05	120	560
10	3	nd	1.3	nd	nd	nd	1	0	0.15	1	0.01	7	740
10	12	nd	27	40	19.0	25	110	0.5	0.11	1	0.00	9	320
12	3	nd	nd	nd	nd	nd	nd	—	0.12	4	0.01	33	—
13	5	nd	nd	nd	nd	nd	nd	—	0.20	110	0.28	550	550
13	16	nd	nd	nd	nd	nd	nd	—	0.20	130	0.34	630	790
13	4	nd	2.2	1.2	0.4	nd	4	0.1	0.23	310	0.41	1400	—
18	4	nd	0.5	nd	nd	nd	0.5	0	0.08	5	0.07	100	—
18	18	nd	2.7	nd	7.3	8.0	18	5.7	0.17	20	0.08	120	—
18	18	nd	1.0	nd	2.4	3.3	6.7	5.7	0.15	26	0.10	170	—
18	30	nd	0.8	nd	nd	nd	0.8	0	0.14	36	0.00	260	—
22	3	nd	nd	nd	nd	nd	nd	—	0.06	1	0.01	17	—
22	8	—	—	—	—	—	—	—	0.05	3	0.01	60	—
22	25	5.8	3.7	0.7	nd	nd	10	0	—	2	0.00	—	330
23 (sewage dump site)	28	nd	1.6	3.2	4.5	3.1	12.1	1.6	0.11	6	0.02	55	1900
24 (dredge dump site)	10	0.6	1.0	3.2	1.2	2.0	8.0	0.8	0.11	6	0.08	55	790
24 (dredge dump site)	3	—	—	—	—	—	—	—	0.05	6	0.03	120	—

level at this station is evidence for the existence of "hot spots" of PAH-rich particulate material. Significant PAH enrichments are observed at midwater at stations 7, 18, 23, and 24. When viewed in its entirety the New York Bight (station 6 and seaward) PAH levels average 1.9 ng/L (range nd−7) in surface waters and 55 ng/L (range nd−370) in mid- and bottom waters.

The PAH compositions found in the study region generally fall into two types, the "light" (group I) assemblage consisting of two- and three-ringed aromatic (naphthalenes and phenanthrenes) compounds and a "heavy" (group II) assemblage which includes four- and five-ringed compounds (chrysene, benzanthracene, benzopyrenes). The fluoranthene−pyrene pair (molecular weight = 202) appears to be a "swing" set in that they are associated with both groupings. Within the estuary, the group II PAH assemblage is found only at stations 1 and 2. Outside of the estuary these aromatics are found at five locations: the midwaters of stations 6, 7, 18, 23, and 24. At the mouth of the estuary, group II PAH are found in the surface water of station 5, sampled at flood tide, and in the surface water of station 4 during flood and high tide.

PCB levels in estuary, bight — PCB in the particulate matter ranged from 0.05 ng/L at station 22 out on the shelf to 3.53 ng/L at station 4 during flood tide. Although not measured, "dissolved" PCB will contain roughly an equiv-

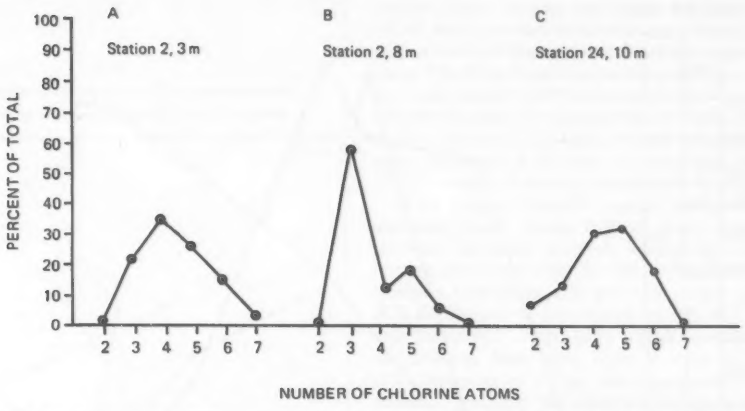

FIG. 3. Representative PCB compositional plots of suspended particles illustrating three main compositional groupings observed in the study area.

alent amount of PCB (de Lappe et al. 1980a, 1980b). Values reported here are substantially lower than bight "background values" previously reported elsewhere (Bopp et al. 1981; Hatcher et al. 1978), but are consistent with recent PCB values in coastal waters from coastal Massachusetts (New Bedford, Buzzards Bay) (de Lappe et al. 1980b) and California (de Lappe et al. 1980a). Our data are two to three orders of magnitude lower than those observed during dumping events involving sewage sludge (Hatcher et al. 1978) and dredged material (Boehm and Fiest 1983) (20–60 ng/L).

On the average the PCB concentrations landward of Rockaway Point are considerably higher than those outside of the estuary. This is especially true of the bottom waters at stations 1 and 2 and station 4 during low tide after particulate material has been swept out of the harbor. In contrast, the PCB levels in the bight proper are quite low and, except at stations 5 and 7, there is little difference in concentration levels between the surface and bottom water at the same station.

PCB levels do not covary with PAH levels in the bight. At locations of elevated PAH levels (e.g. stations 6, 10, 18, 23, 24), PCB levels remain relatively invariable. Only at station 7 do PAH and PCB levels increase in midwaters (10 m), although PCB increased only a modest three- to four-fold, while PAH increased at least 10-fold.

Particulate PCB in the water column from several key stations are of three main PCB compositions (Fig. 3). The first type (Fig. 3A), the most frequently encountered PCB composition with a maximum of tetrachlorobiphenyl isomers, is characteristic of sewage effluents in the estuary (MacLeod et al. 1981). Note that although the PCB levels change markedly during the tidal cycle at station 4, the PCB composition does not. The second major PCB compositional type (Fig. 3B) was observed in the bottom waters of the inner harbor region where trichlorobiphenyl isomers and, to a lesser extent pentachlorobiphenyls, dominated. This bimodal distribution is linked to Hudson River sediment resuspension in that the upper Hudson River sediments are impacted by Aroclor 1016 which has abundant trichlorobiphenyl isomers originating in an upriver industrial source (Bopp et al. 1981). The trichlorobiphenyl-dominant and bimodal distributions are also found in the entire water column at station 18 and at station 10 at 10 m. The third distribution (Fig. 3C) with constituent maxima in the pentachlorobiphenyl and tetrachlorobiphenyl region is characteristic of bottom or intermediate waters at stations 6, 7, and 24 and may be associated with resuspension of waste deposit sediments.

Surface vs bottom water of the inner harbor — At stations 1 and 2 in the Inner Harbor area there is a marked vertical stratification of particulate PAH, PCB, and coprostanol, both in concentration and in composition of the compound groups present. Elevated PAH and PCB concentrations were observed in the bottom water in spite of the surface water's higher suspended load (Table 1). Surface waters at these stations contain elevated coprostanol concentrations.

PAH levels in the bottom waters at stations 1 and 2 are considerably higher than those in the surface waters (3 m, $\bar{x}$ = 11.5 ng/L; 8 m, $\bar{x}$ = 25.5 ng/L). PAH levels in the inner harbor are not coupled with the TSM which is higher in the surface water (station 1, 2350 vs 1750 μg/L). Only at stations 1 and 2 in the lower Hudson River do we find the group II and group I PAH groups in the same samples. At all other stations, two independently behaving groups of PAH are observed.

PCB levels are also higher in bottom waters (x = 80 ng/L) than in the surface waters (x = 34 ng/L) in spite of the apparent well-mixed state of the water column, as evidenced by hydrographic data (J. Bisagni, NOAA-NOS, Naragansett, RI, personal communication). As with the PAH concentrations, the PCB levels are not coupled with the TSM. As well as having different concentrations, the PCB compositions of the surface and bottom waters differ. In the surface waters at stations 1 and 2 the tetrachlorobiphenyl isomer group is clearly dominant, with the pentachlorobiphenyls and

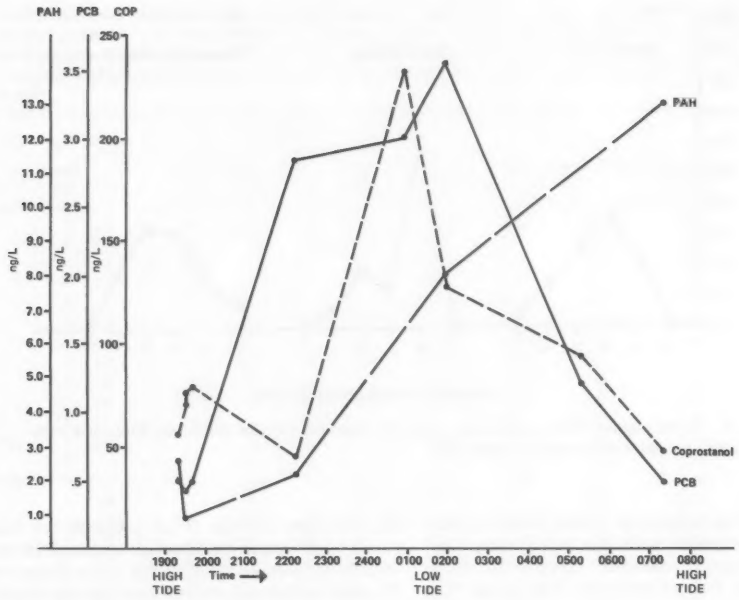

FIG. 4. Particulate organics in tidal time series at station 4.

trichlorobiphenyls present as the second and third most dominant isomer groups, respectively (Fig. 3A). This is quite different from the PCB isomer distribution in the bottom waters of the inner harbor where the trichloro isomer group is strongly dominant and a bimodal distribution is observed (Fig. 3B). Thus, resuspension of Hudson River sediment apparently affects bottom waters only, with surface waters influenced mainly by various sewage treatment plant effluents having the tetrachlorobiphenyls as their major PCB compounds.

Tidal time series at station 4 — The surface water of station 4, just inside the mouth of the estuary, was sampled eight times through the course of a complete tidal cycle. Through the ebb part of the cycle and during the low slack water, PAH concentrations remained quite low (1–3 ng/L) and were of the group I variety. However, concentrations increased during the flood tide (8 ng/L) and peaked at high slack water (13 ng/L). Although not sampled, bottom waters may have had different PAH concentrations during this peak in surface water PAH concentrations. However, the water column at station 4 was very well mixed according to hydrographic data. During the ebb and low tide periods, the PAH composition consisted only of tricyclic (phenanthrenes) and one tetracyclic (fluoranthene–pyrene) homologous series (Table 1). The PAH material carried to this station from the seaward direction during the flood tide was enriched in the tetracyclic and pentacyclic PAH compounds (PAH group II). Note that waters at station 5 at the mouth of the estuary are characterized by the presence of group II aromatic compounds.

At stations 1 and 2, the tetracyclic and pentacyclic compounds are present both in the surface waters (3 m) and in the near-bottom waters (8 m). In the surface water at station 3, also in the upper bay, no group II PAH compounds are present and only small quantities of group I and PAH "swing" compounds (fluoranthene–pyrene) were present. At station 5, which was sampled during flood tide (approximately 1 h from high tide), pentacyclic PAH compounds are found only in the surface water, while group II PAH reside in bottom waters just seaward at station 6. As discussed later, these data from stations 4, 5, and 6 suggest a landward transport of group II PAH.

The behavior of PAH during the sampled tidal cycle at station 4 is unlike that of the PCB and coprostanol observed during the same time period (Fig. 4). While PAH levels increase during the flood tide, PCB and coprostanol concentrations increase as the tide ebbs, reaching their highest concentrations (PCB, 3.53 ng/L; coprostanol, 233 ng/L) at low tide and in the slack tide just after dead low tide.

Although absolute PCB levels at station 4 change dramatically during the course of the tidal cycle, the composition of the PCB is remarkably constant, with the tetrachlorobiphenyls dominant throughout the sampling period (see Fig. 3A).

Coprostanol levels — Coprostanol data from the inner estuary and obtained during the tidal cycle time series at

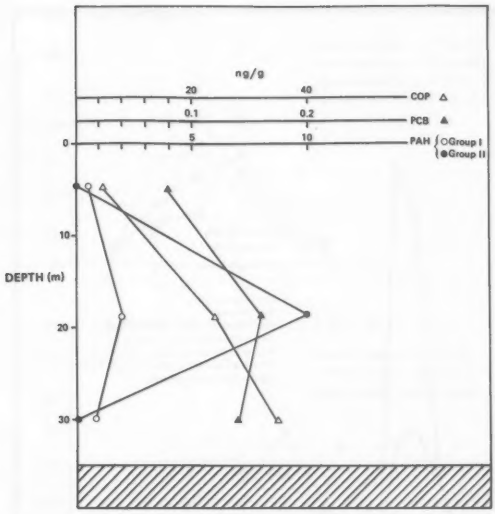

FIG. 5. Vertical water column profiles of particulate organic compound concentrations (station 18, head of Hudson Valley) illustrating lack of covariance of PAH and other organic classes.

station 4 are presented above and in Table 1. At station 13, which was sampled twice in 3 d, coprostanol levels both in the surface and near-bottom waters were consistently high ($\bar{x}$ = 182 ng/L), approximately an order of magnitude greater than the levels at the surrounding stations (24, 18, and 7) and comparable with those in the surface waters of the inner estuary where the concentration of sewage-related material is probably greatest.

The significant increase in coprostanol levels at station 13 (110–310 ng/L) was not accompanied by a concomitant PCB or PAH increase. The linkage of surface waters with seaward flowing estuarine–harbor sewage effluents is confirmed by the coprostanol distributions. Coprostanol levels vary from 50 to 200 ng/L in the inner harbor, with the maximum levels found in the surface waters. Note that the absolute PAH and PCB concentrations are greater at the bottom than at the surface, illustrating decoupling of these compounds. Clearly, the trichlorobiphenyl and coprostanol distributions do not covary in the lower river system. The tetrachlorobiphenyls and pentachlorobiphenyls and coprostanol do appear to covary by virtue of their common origins (i.e. sewage effluents). Both PCB and coprostanol are known to be environmentally "resistant" compounds, indicating low comparative oxidation (Walker et al. 1982). The relative oxidative susceptibility of the various compound classes is unknown.

Vertical distributions of PAH, PCB, and coprostanol offshore — A variety of surface-to-bottom trends in particle-bound compounds are encountered in the bight. In general, PAH distributions vary vertically more than do PCB or coprostanol levels. For example, while surface waters at station 5 contain more PAH (and PCB) compounds than subsurface waters, the mid- and bottom waters at stations 6, 7, 10, 18, and 22 contain elevated levels of PAH compared with surface waters at these stations. Equal amounts of group I and group II PAH are found in subsurface waters at stations 10 and 22, while Group II PAH are more abundant at stations 7 and 18 (see the group II to group I ratio in Table 1). PCB levels at 10 m at station 7 are higher than at the surface, indicating some covariance with PAH, yet very high PAH levels at 10 m at station 10 are not accompanied by PCB increases.

At the deeper station 18, vertical profiles exhibit several interesting trends. Group II PAH clearly show a profound midwater maximum at 18 m, while coprostanol increases linearly with depth (Fig. 5). The coprostanol to PCB ratio increases with depth, thus suggesting that coprostanol and PCB distributions do not strongly covary. It is interesting to note that the PCB compositions at all of the station 18 samples are different from other bight samples in that the trichlorobiphenyls are slightly more concentrated than the next abundant grouping, the tetrachlorobiphenyls. Remnants of a recent dredged material or sludge dumping event or resuspension of the silt fraction of deposited sewage sludge are suggested as possible sources. Note also that a prominent bimodal (trichlorobiphenyl and pentachlorobiphenyl maxima) PCB compositional distribution is noted at station 10 (10 m) where a large pulsed PAH input is apparent.

The vertical distributions of compounds at station 13 indicate higher surface water concentrations of coprostanol and in one case (the station was visited twice) elevated PAH levels. However, the entire station 13 water column remains elevated in coprostanol levels. PCB levels were only slightly elevated (0.2 ng/L) in all cases (Table 1). However, in only one sample were PAH compounds detected at all.

CHEMISTRY OF WASTE DEPOSITS

Important quantitative and compositional differences are revealed when considering size fractions within sedimentary deposits (Thompson and Eglinton 1978). In the present study, significant chemical differences were observed in the dredged material core and in the sewage sludge deposit in (1) gross organic parameters, (2) PAH levels, (3) PCB levels, and (4) coprostanol levels. These quantitative and qualitative differences are summarized below and are presented in more detail elsewhere (Boehm 1981).

On a dry weight basis the sewage sludge material is richer in organics than the mud layer (4.5–9.0 cm) of the dredged material core. The sewage contains over four times as much extractable organic material (14 vs 3 mg/g), seven times as much saturated hydrocarbon material (4.8 vs 0.7 mg/g), and almost five times as much aromatic material (2.5 vs 0.5 mg/g). As the grain size decreases, the associated absolute organic compound concentrations increase. The association of organic material with fine particles is dramatic. It is these particles that are most easily resuspended in the water column above. For example, in the top (0–4.5 cm) sandy layer of the dredged material deposit, 70% of all the organic material is associated with the 3% of fine material. Similarly, in the dredged material and sewage sludge mud layers, about 62% of the organics are associated with the 13–24% of fines.

Sewage sludge is "rich" in PAH compounds (total

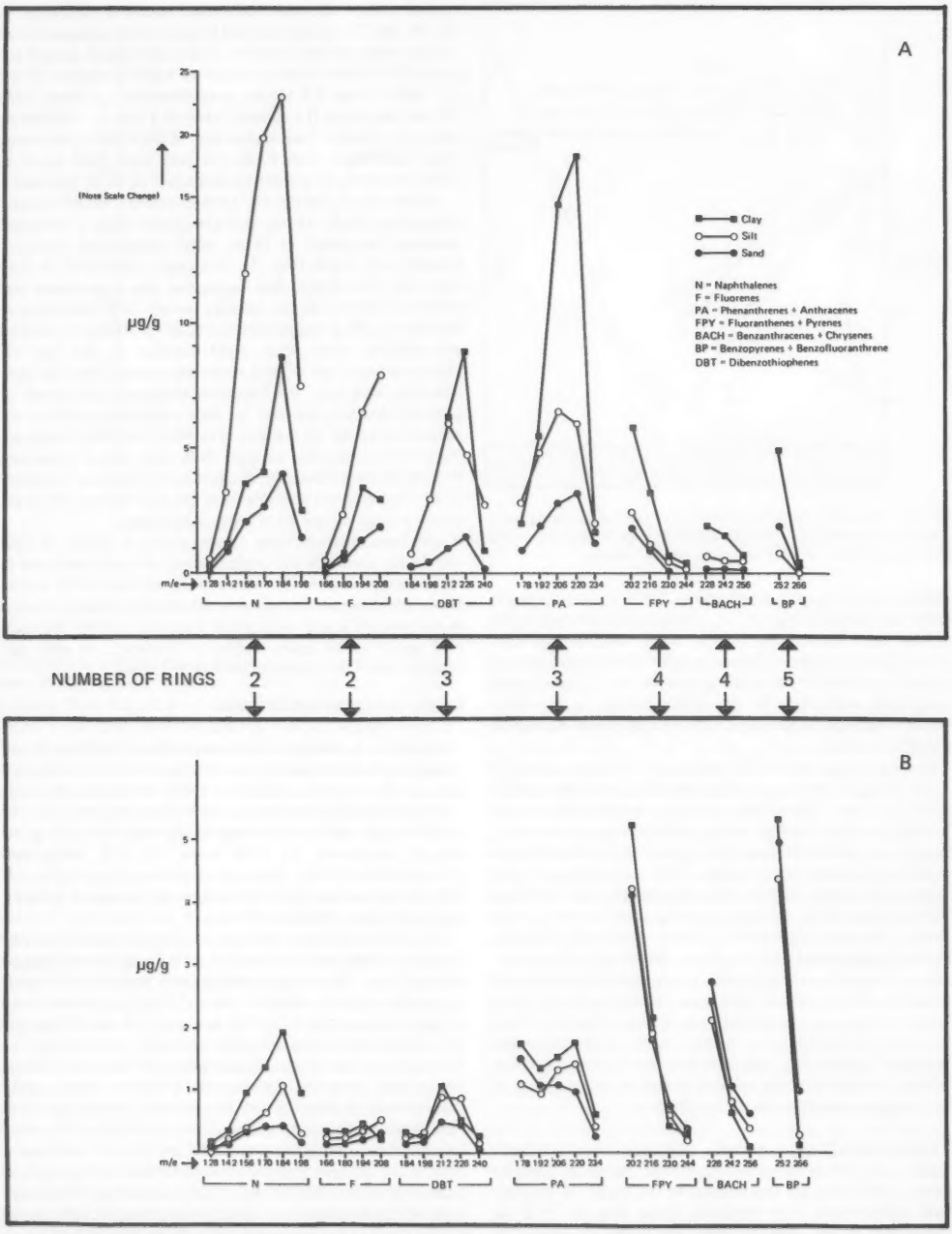

FIG. 6. PAH alkyl homologue distributions showing (A) sewage sludge, mainly fossil fuel derived, and (B) dredged material, mainly combustion derived. Within each homologous series, numbers represent molecular weights of parent compounds (unsubstituted), methyl, dimethyl, etc., compounds (e.g. 128 = N, 142 = C_1N, 156 = C_2N, etc.).

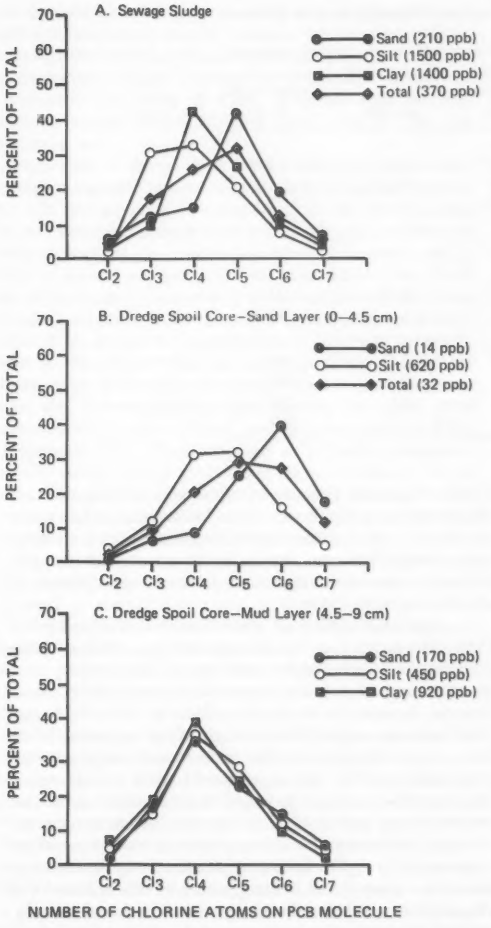

FIG. 7. PCB composition of size fractions of (A) sewage sludge and (B, C) two layers within the dredged material core.

47.3 μg/g = parts per million). This value is much higher than "background" or non-waste-deposit values determined in the New York Bight sediments (50–500 ng/g = parts per billion) (Boehm 1980a). However, the actual sediment association of the PAH compounds is revealed in Fig. 6A where the PAH distributions in each sediment fraction are detailed.

In the sewage sludge deposit (Fig. 6A) there are large PAH concentration differences among the three size fractions. These differences must be analyzed on a compound series by series basis. For example, while the naphthalene and fluorene compound series are more strongly associated with the intermediate size particles (i.e. silt), concentrations of the dibenzothiophenes are roughly equivalent in the silt and clay size particles. Highest concentrations of phenanthrenes are strongly associated with the fine clay particles. The four- and five-ringed aromatic compound series are found associated to a greater extent with clay than with either silt or sand. In contrast, the PAH compounds in dredged material (Fig. 6B) are predominantly the tetracyclics and pentacyclics, with lesser amounts of the two- and three-ringed compounds present. Although variations between the different fractions are present, these are minor compared with the size variations in the sewage sludge material examined.

Concentrations of PCB within the sewage sludge deposit (overall 367 ppb) range from 208 ppb in the sand fraction to 1450 ppb in the silt fraction (Fig. 7). The clay fraction is of equivalent concentration (1370 ppb). Clearly, a strong association of PCB with the finer sediment particles is evident. This association appears most pronounced for the tetrachlorobiphenyls and trichlorobiphenyls (Fig. 7) which are associated with both the silt and clay fractions, albeit differentially with the two fractions. The more highly chlorinated PCB are associated with the sand fraction to a greater relative extent (Fig. 7). These compositional details, which clearly indicate both qualitative and quantitative fractionations within the sewage sludge bulk sediment, are completely obscured when the overall composition is assessed (Fig. 7). In the latter case the pentachloro PCB are most abundant, followed closely by the tetrachloro PCB, with distribution commonly associated with an Arochlor 1254-type formulation. The compositions within the dredged material size fractions (Fig. 7C) are remarkably constant, with the tetrachloro PCB isomers clearly dominant in all size fractions. Again, in contrast with sewage sludge, PCB in the dredged material show no qualitative differences of grain size (Fig. 7), with the tetrachlorobiphenyl isomers dominant in each size fraction. Quantitatively, more PCB material is associated with the fine fraction.

Data on the concentration of coprostanol and that of coprostanol relative to the major sterols and stanols of mixed planktonic–sewage (cholesterol, cholestanol) and planktonic (stigmasterol, β-sistosterol) origins, shown in Table 2, indicate that the absolute concentrations of coprostanol and the coprostanol to total steroid ratio are higher in the sewage sludge relative to dredged material. The ratios of coprostanol to total steroids and coprostanol to PCB have been considered before (Hatcher and McGillivary 1979; Boehm 1980a) and serve as key diagnostic ratios to discern the sources of sedimentary pollutants. The ratio is invariable within the size fractions of each sample although the absolute coprostanol level is high in the fine fraction. The coprostanol concentration in the overall bulk sewage sludge is 94 ppm (420 ppm in the clay fraction), while it is only 2.7 ppm in the dredged material mud (12 ppm in the clay fraction). Both the dredged materials and sewage sludge are abundant in PCB compounds. However, the strong association of coprostanol with sewage sludge serves to differentiate these two main possible sources of suspended particulate PCB in the overlying waters.

Discussion

The PAH concentration data presented here represent one of the very few data sets on PAH levels in nearshore and open ocean waters. Readman et al. (1982) examined PAH levels and composition in the Tamar Estuary and found individual PAH levels to range from 1 to 50 ng/L. These authors also

TABLE 2. Concentrations of coprostanol and key diagnostic ratios in sediment size fractions.

	Coprostanol (μg)	Coprostanol/ concentration (μg/g)	Coprostanol/ total steroids	Coprostanol/ PCB
Dredge (sand)				
Sand	5.5	0.07	0.07	8.0
Silt	6.4	2.5	0.03	7.2
Total	11.9	0.14		7.5
Dredge (mud)				
Sand	42.2	1.3	0.32	13.4
Silt	29.3	4.3	0.39	12.5
Clay	47.7	12.2	0.38	21.6
Total	119.2	2.7		15.3
Sewage				
Sand	440	60	0.7	190
Silt	140	230	0.6	180
Clay	220	420	0.6	230
Total	800	90		200

discerned the independent behavior of two groups of PAH compounds, as is reported here.

A wide range of PCB concentrations in the water column have been reported (see National Academy of Sciences 1979). Those reported here (0.1−4 ng/L) covering nearshore (0.1−0.7 ng/L) and estuarine (0.2−4 ng/L) areas are lower than those observed during and shortly after dumping events (Hatcher et al. 1978; Boehm and Fiest 1983) but agree with similar sets of nearshore background data obtained by de Lappe et al. (1980a, 1980b). If one evaluates the "worst case" and assumes that all suspended matter in New York Bight (1 g suspended matter/L) (R. Mukherji, University of Rhode Island, personal communication) originates from resuspended sewage sludge (0.5−2 mg/g PCB) (West and Hatcher 1980; Boehm 1980a), then maximum water column particulate PCB levels would be 0.5−2 ng/L. Clearly, any values greater than 2.0 ng/L in the bight apex proper during nondumping conditions must be considered carefully (during dumps of sewage sludge and dredged material, PCB concentrations are observed in the 30−60 ng/L range) (Hatcher et al. 1978; Boehm and Fiest 1983).

The process of piecing together the organic chemical data and relating PCB, PAH, and coprostanol distributions to suspended particulate sources is one that must be undertaken with an awareness that while all of these chemical classes are constituents of all of the major pollutant sources to the estuary/shelf system, their geochemical behavior and hence their areal distributions are not necessarily coupled. This became apparent in the evaluation of the data sets in which there are many examples of elevation of one component class with minimal corresponding variance of another class. Three notable examples of this concern PCB distributions at stations 1 and 2, coprostanol distributions at station 13, and PAH distributions at station 10.

In the first case we see markedly elevated PCB levels in bottom waters undoubtedly related to resuspension and downstream transport phenomena within the Hudson River system. The elevated PCB levels are accompanied by only a modest PAH increase and virtually no coprostanol increase. Indeed, the sewage input can be seen instead in the near-surface water at stations 1 and 2 where the PCB concentrations are lower, their composition maximum is in the tetrachlorobiphenyls, and where abundant coprostanol from sewage effluents is clearly observed (Table 1).

A significant increase in coprostanol levels at station 13 (110−310 ng/L) was not accompanied by a PCB or PAH increase. The coprostanol to total steroid ratio initially suggests an input of particulate matter from the nearby dredged material deposit. However, the relatively minor PCB and PAH increases suggest that the origin of this coprostanol-rich water may be from the estuarine surface waters where both the coprostanol-to-PCB and coprostanol-to-total steroid ratios approach the corresponding values observed at station 13. The observation at station 13 is of considerable interest, as the elevated coprostanol levels were observed on two occasions separated by 3 d. The linking of station 13 organic constituents to estuarine fluxes is strengthened by observations of a characteristic southward flowing plume along the New Jersey coast of estuarine water impinging on the region of station 13 (Freeland and Swift 1978; Gadd et al. 1978; D. Kester and R. Mukherji, University of Rhode Island, personal communication). Any minor point sources of sewage effluent along the New Jersey coast can probably be neglected due to the dilution of these minor effluents prior to possible transport to station 13.

At stations 10 and 7, marked elevations in PAH levels linked to the group II PAH source(s) are either weakly linked (station 7) or not at all linked (station 10) to PCB or coprostanol levels. The set of values observed at station 7, closer to the mouth of the river−harbor region, suggests a mix of estuarine water (source of much of the coprostanol and PCB material) and an offshore source of group II PAH, perhaps from a dredged material source which exhibits abundant group II PAH profiles. The origin of PCB composition at station 7 is not entirely clear, but a combination of estuarine (tetrachlorobiphenyl-dominant source)

and dredged material (tetrachlorobiphenyl- and pentachlorobiphenyl-dominant source) sources is one possibility. Although the PAH distributions in the particles at the entrance to the estuary suggest landward bottom water transport of dumpsite-related group II PAH, it is not clear whether dumpsite-related PCB are being transported towards the estuary as well.

The origin of the group II PAH distribution in the water column is linked to resuspension of dredged material deposits through two pieces of information. First, the bottom water (10 m) particulate sample from station 24, adjacent dredged material disposal site, contains moderately elevated levels of PAH in general and group II PAH in particular. Such PAH distributions are limited to only a few samples outside of the estuarine area (see Table 1) but notably impact intermediate-depth water at station 7, approximately 7.5 km to the northwest of the dredged material dumpsite. Second, the PAH distributions in the dredged material deposit in all size fractions are characteristically dominated by pyrogenic PAH compounds (i.e. three-, four-, and five-ringed parent PAH compounds (Fig. 6B) as opposed to a largely petroleum-derived sewage sludge PAH distribution). However, the resuspension of fine sewage sludge particles followed by the rapid loss due to solubility of the two-ringed aromatics can also account for the group II PAH distribution.

For the most part, the naphthalene, fluorene, and dibenzothiophene homologous PAH compound series (group I) in sewage sludge and dredged materials are attributable to petroleum inputs, while the fluoranthene−pyrene, benzanthracene−chrysene, and benzopyrene series (group II) largely originate in pyrogenic combustion of fossil fuels (Blumer 1976; Brown and Weiss 1978; Farrington 1980; Lee et al. 1977). In addition, PAH of a petroleum origin will be dominated by the more highly alkylated members of each homologous series, while PAH of pyrogenic origin will be dominated by the parent compound in each homologous series, with lesser amounts of alkylated substituents (Youngblood and Blumer 1975; Laflamme and Hites 1978). The phenanthrene−anthracene series is found in PAH assemblages of both petrogenic and pyrogenic origin (Tripp et al. 1981; Lee et al. 1977) although, again, the parent compound − alkylated compound associations with the various sources prevail and act as source indicators.

The great abundance of naphthalenes, fluorenes, and dibenzothiophenes in the sewage sludge along with the preponderance of higher alkylated phenanthrenes (Fig. 6A) strongly suggest a dominant petroleum source for the sewage sludge PAH compounds. We estimate on the basis of the areas under the curves of Fig. 6 that 85−90% of PAH found in the sewage deposit sample originates in fossil fuel sources with (see Fig. 6 for abbreviation key)

$$\% \text{ petroleum} = \frac{\Sigma(N + F + DBT + 1/2P)}{\Sigma(N + F + DBT + P + FPY + BACH + BP)}.$$

Dredged material PAH, on the contrary, are strongly linked to pyrogenic sources due to dominance of tetracyclic and pentacyclic PAH compounds (Fig. 6). Thus, the PAH−size associations differ remarkably between the dredged material and the sewage sludge material. The shape of the phenanthrene series (Fig. 6B) composition in all size fractions is interesting. The inflection at C_1 phenanthrene with a subsequent C_3 phenanthrene maximum for all size fractions strongly suggests a composite (pyrogenic and petrogenic) source of tricyclic aromatics in this sample.

Down-valley transport of particles bearing organic chemicals from station 23 in the Christaensen Basin to station 22 farther out on the shelf and in the Hudson Valley channel is suggested by the anomalous trichlorobiphenyl abundance in the station 18 water column and the petrogenic nature of the PAH material at both stations (i.e. lighter two- and three-ringed PAH with some four-ringed influence, but no group II PAH). The origin of this PAH material appears to be linked to sewage sludge by virtue of similarities in PAH compositional distributions and the obvious benthic source of water column coprostanol at station 18. Coprostanol values at station 22 are quite low, however, and PCB information is spotty. Thus, the postulation of down-valley transport of sewage-related organics is speculative at this point although sedimentary coprostanol levels in the valley and out to the shelf break appear to indicate such net transport (Boehm 1980a).

Particle transport at the entrance to the estuarine−river area is quite complicated (stations 4, 5, 6). The time series at station 4 reveals that surface waters are profoundly influenced by the tidal movement of PAH-rich particles from the seaward direction and PCB- and coprostanol-bearing particles from the estuary. If we look at the data from station 5 at which both surface and bottom water particles were obtained we see PCB- and PAH-rich particles at the surface. Stations 6 and 7 are closely linked to each other by virtue of elevated midwater (10 m) PAH levels at station 7 and elevated bottom waters PAH levels at station 6 (12 m). As substantial levels of group II PAH are observed at midwaters at stations 6 and 7, the station 5 surface increase is most likely due to bottom to surface mixing of a patch of PAH-rich water into the surface waters.

Station 4 data indicate that the PCB and coprostanol concentrations covary, while PAH acts independently. In addition to the sewage-related PCB and coprostanol, perhaps the group I PAH compounds are transported seaward through the ebb tide, while group II PAH are brought into the estuary from offshore during the flood tide. Thus, a two-layer estuarine transport system (Duedall et al. 1979), wherein less dense river water flows out of the estuary on the surface, causes the sewage-associated particles with their PCB and coprostanol loadings to be transported seaward. Note at station 5 that surface water coprostanol levels (160 ng/L) are much greater than bottom water levels (6 ng/L). Nutrient levels observed at the mouth of the estuary by Duedall et al. (1979) were also linked to seaward transport of sewage-related material. Tetrachlorobiphenyls, the dominant PCB distributed throughout the entrance to the estuary, probably are linked to sewage effluents as opposed to the trichlorobiphenyl-rich Hudson River bottom sediments. In sewage sludge, pentachlorobiphenyls are dominant overall, but tetrachlorobiphenyls dominate the fine fraction, which is most easily resuspended and transported out of the estuary, evidently in surface waters.

During the study, transport in subsurface waters near the

TABLE 3. Approximate compound solubilities.

Compound	Solubility (μg/L)	Reference
PAH		
Phenanthrene	~1000	May (1980)
Fluoranthene	~220	May (1980)
Pyrene	~150	May (1980)
Benzanthracene	~10	May (1980)
Chrysene	~2	May (1980)
Benzopyrenes	~0.5	Inferred
PCB		
Aroclor		
1016 (Cl_2, Cl_3, Cl_4)	906	Griffin and Chian 1980
1242 (Cl_2, Cl_3, Cl_4, Cl_5)	703	Griffin and Chian 1980
1221 (Cl_1, Cl_2, Cl_3)	3516	Griffin and Chian 1980
1254 (Cl_3, Cl_4, Cl_5)	70	Griffin and Chian 1980

mouth appeared to be in the landward direction with a bight apex origin for elevated group II PAH observed in mid- and bottom waters and for the elevated group II PAH compounds appearing at station 4 during flood tide. The absence of group II PAH in station 5 bottom waters is anomalous but may be attributable to patchiness in the system.

One should realize that the observations at all stations, other than 4 and 13 where some time series information exists, are essentially geochemical and oceanographic "snapshots." One envisions surface water and bottom water patches of particles bearing organic pollutants whose ultimate fate and transport is determined over many tidal cycles and which are highly dependent of the bight circulation. Clearly, several tidal cycles are required to define the PAH "story" at station 4 where PAH levels are low at the initial sampling (just after high tide) and do not return to these levels over the tidal cycle observed.

The covariance of PCB and PAH levels in the water column will tend to be strongest where suspended particle densities are greatest (i.e. stations 1 and 6) and where a common source for the two compound classes exists. Covariance is the exception in this study rather than the rule. The situation at stations 1 and 2 well within the harbor is clearly dominated by differential sewage effluent and resuspended Hudson River sediment sources. However, the situation at stations 6 and 7 is less clear. The data from those stations point to a loss of PCB from suspended particles regardless of what the ultimate source of offshore suspended pollutants is. PCB materials are more soluble in water than the benzanthracenes, chrysenes, and benzopyrenes and more soluble than the other tetracyclic PAH (fluoranthene and pyrene) as well (Table 3). PCB do have a great affinity for solid surfaces with their adsorption strongly linked to the organic carbon content of adsorbing substances (Griffin and Chian 1980). Thus, nonrecent (hours to days) resuspension of waste deposit material offshore followed by aqueous transport in areas of low suspended matter may result in the differential partitioning of PCB and PAH into the dissolved phase, with dissolution affecting these compounds in the order phenanthrene > PCB ≥ fluoranthene–pyrene > benzanthracene–chrysene > benzopyrenes. Apparent decoupling of PCB and group II PAH may then be the result of transport away from an offshore source, followed by selective PCB dissolution.

As stated by Freeland and Swift (1978) the regional fine sediment budget of the estuarine – New York Bight – shelf system is very complex. An exchange of suspended material between the "turbid water masses of the inner shelf, New York Harbor and associated bays . . ." occurs through every tidal cycle. Duedall et al. (1979) describes the tidal currents through the lower bay complex and estuary mouth as reaching 5.5 km/h (3 kn), quite sufficient for resuspending material in the mouth area and driving it landward or seaward depending on the tidal vector. Ocean dumping events do not have a profound lasting (>6–12 h) effect on the region's suspended particulate organic chemistry, as the bulk of the dumped material is rapidly sedimented. However, the long-term residence of fine particles in the water column from ocean dumping events, hitherto undetected due to extreme patchiness or lack of instrumental sensitivity, cannot be ruled out as impacting the trace organic chemistry of the bight.

Storm-induced resuspension may play a dominant post-dumping role in introducing resuspended waste deposit sediments into the bight water column. Indeed, a storm impacted the study area on August 21, prior to much of the sampling. Thus, the existence of "patches" of PAH-rich material with elevated PCB levels offshore may be at least partly attributable to storm-induced resuspension phenomena.

Thus, the fluxes of suspended particles bearing organic chemicals may be summarized as follows (illustrated in Fig. 8).

1) In the New York Harbor – Hudson River area, PCB-rich sediment is resuspended. Our data do not reveal net seaward transport of this resuspended material.
2) Sewage effluent material is confined to surface layers in the inner harbor – river area and may be transported substantial distances seaward as part of a classical two-layer estuarine stratification system characteristic of the region and following coastal circulation patterns (Freeland and Swift 1978; Hansen 1978; Duedall et al. 1977). A seaward flux calculation can be made using data presented here which indicate that if estuary water (3 ng/L PCB) is transported out of the estuary in the surface (2 m) waters through the Rockaway Point – Sandy Hook transect and with a mean current velocity of 3.7 km/h (2 kn) (Duedall et al. 1979), ~2.7 kg of PCB is transported out of the estuary daily. This compares to a "standing crop" of ~6.0 kg of PCB in the bight apex (average PCB concentration taken as 0.3 ng/L in 20 m of water in a 1000-km^2 area).
3) Resuspended particles rich in higher molecular weight PAH are transported at depth from the inner bight apex to the mouth of the estuary (Rockaway Point) during flood tide.
4) PAH-rich, PCB-depleted particles resuspended from dredged material deposits are found in mid- and bottom waters in patchy distributions in the bight area.
5) Resuspended sewage-associated particles occur near the dumpsite and may be transported down the Hudson Valley in mid- and bottom waters.

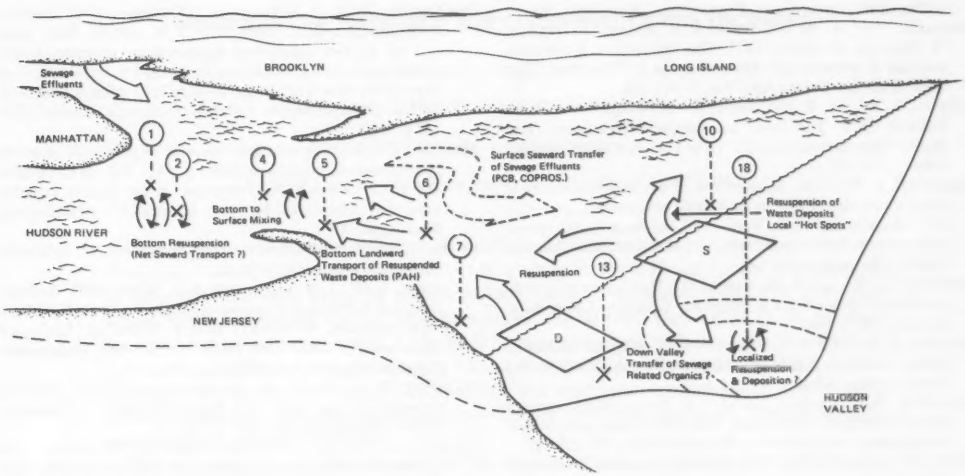

FIG. 8. Organic pollutant resuspension and transport systems as suggested by the data (numbers refer to stations; broken-line arrows represent surface transport; solid-line arrows represent bottom or midwater transport).

Acknowledgments

The following people played important roles in the sample acquisition and generation of the organic chemistry data forming the basis of this report: Tom Dorsey, Scott Drew, John Yarko, David Fiest, Diana Pilson, Neil Mosesman, and Ann Jefferies, all of ERCO. The coordination and execution of the research cruise was a result of the considerable efforts of Dr. Tom O'Connor (NOAA). Exchange of ideas and data between the authors and Drs. Dana Kester and Raj Mukherji were very helpful as was the critical review by Dr. James Quinn, all of the University of Rhode Island. This project was supported mostly through NOAA research grant No. NA-80-AA-D-00062 from the NOAA Office of Marine Pollution Assessment.

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Session III — Summary and Overview: Ocean Dumping

MICHAEL A. CHAMP

The American University, Washington, DC 20016, USA

AND JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

No discussion of oceanic pollution is complete without mention of the subject of ocean dumping, that is, the practice of transport of a waste material to sea for the sole purpose of disposal. The wide range of wastes include dredged materials, municipal and other urban wastes, industrial wastes, sewage sludge, and so forth (see Table 1). In general, dumping is regulated by permits. Over 2000 permits are issued annually, on a global basis. As recorded with the London Dumping Convention, this increases at a rate of 80 permits per year. For the North Atlantic Ocean alone, this represents approximately 135×10^6 t of waste materials, in which the major constituents are dredge materials, sewage sludge, and industrial wastes (Table 2).

The four papers on ocean dumping in this session record some of the results of studies on the fate of waste material at one Atlantic Ocean dumpsite, Deepwater Dumpsite 106 (DWD 106). So called because of its distance from the entrance to New York Harbor (approximately 106 mi), DWD 106 is located on the continental slope of the northwestern Atlantic Ocean, with water depths ranging from 1500 to 2700 m. The oceanographic regime is complex, with strong oceanic frontal dynamics. While not affected directly by the Gulf Stream, which lies approximately 10 km southeastward, the area is frequently traversed by warm-core eddies that spin off from the Gulf Stream. These add to the complexity of the system by both enhancing the mixing processes of the dumpsite area and by replacing slope water that normally forms part of the shelf system (see Wiesenburg and Brooks, this issue).

The dispersive and mixing processes at the DWD 106 are examined in two papers, Wiesenburg and Brooks and O'Connor et al. O'Connor et al. develop a model for the physical dispersion of sewage sludge, based on sludge composition and the factors of volume, discharge rates and seawater fluxes through the area, and focus on the projected residence times and fate of PCBs, PAHs, and some metals. Their calculations indicate the formation of a plume of contaminants stretching from the discharge point over a 60-km-wide area between the site and the southeastward Gulf Stream. However, this plume, with an Fe, Pb, Zn, Cr, and PCB content, would be largely contained in a 20-m-deep mixed layer, effectively separated from the deeper shelf waters and the underlying benthic sediments. Entry into those lower levels of the system would depend on sedimentation of particulate materials, primarily those sinking at 10^{-2} cm/s or faster. The authors suggest a minimum adverse impact on phytoplankton and zooplankton in the plume, arguing that the very rapid dilution would, by either incoming shelf water or by warm-core eddy mixing, force contaminant concentrations well below established acute lethal toxicity levels (LC50) for these organisms. Most of the long-term contamination is seen to result from PCBs and PAHs that become sedimented out, but it is estimated that maximum concentrations in the benthos would not go over 0.2–0.3 μg/g (ppm).

In their dye study, Wiesenburg and Brooks focus on one of these compartments, the surface waters, by tracing the fate of volatile organics in DuPont Grasselli and American Cyanamid waste when dumped into this system. Not unpredictably, the concentrations in the water column drop off very rapidly, presumably because of the high toluene (approximately 85%) and other low molecular weight and volatile organics content. Dilution is calculated to account for the reduction in concentration by a factor of 1300. Other mixing processes and evaporation are thought to add another factor of 1000 to this, dropping the contaminant load to near background levels within 24 h.

Printed in Canada (J7363)
Imprimé au Canada (J7363)

TABLE 1. Categories of wastes ocean dumped. (From M. A. Champ and P. K. Park. 1982. Global marine pollution bibliography: ocean dumping of municipal and industrial wastes. Plenum Press, New York, NY. 399 p.)

Municipal wastes
Sewage sludge
Solid wastes (cellar dirt)
Garbage–baled refuse
Building–construction debris
Industrial wastes
Acid
Alkaline–organic wastes
Containerized waste
Coal wastes (colliery, fly ash, scrubber sludge, and bottom boiler ash
Cryolite (aluminum) sludges (red muds)
Dredged materials
Drilling fluids–muds and cuttings
Fish (seafood) wastes
Munitions
Ocean mining wastes
Petrochemical wastes
Pharmaceutical wastes
Radioactive wastes

Capuzzo, on the other hand, discusses the role of sedimentation, as enhanced by biological intervention (fecal pellet production) in carrying contaminants out of the surface waters to the deeper waters. Beginning with samples of DuPont Edgemoor waste, an acid-iron waste derived from titanium dioxide production and containing high levels of various trace metals, she determined experimentally the accumulation of a range of metals by zooplankton (copepods) and the subsequent enhancement of metal cycling through the copepods into the fecal pellets. With fecal production in these waters constituting a major biological process in sedimentation, it would seem that metal deposition through this route becomes a major factor in transporting metals such as Fe, Pb, Ni, and Cu from the surface waters to the benthos.

Interestingly, not all metals appear to behave alike. Thus, while Fe, Pb, Ni, and Cu clearly were cycled through the copepods into the fecal pellets, Cd could not be detected in the pellets. Also, these various metals would seem to enter differentially into the zooplankters: Fe and Pb via ingestion of particulate matter, Cu via a combination of particulate ingestion and diffusion, while the results of Cd measurements favor a diffusion route only.

It is becoming increasingly and obviously clear that we must underline two essential principles in considering coastal contamination: all physical and chemical aspects of coastal dynamics and processes and the need for long-term studies. The DWD 106 site is only one of several dumpsites for waste from the New York region, albeit the most distant and deepest. But input also comes from contaminant materials transported out of the Hudson–Raritan river and estuarine system. Thus, contaminants have multisource origins, and understanding the coastal pollution processes therefore requires an understanding of contaminant coupling between the riverine–estuarine system and the shelf–offshore system, as well as the processes occurring on the shelf per se.

In this context, Boehm describes the pathways of three contaminant groups: PCBs via the bottom currents in the estuary, PAH compounds, and the fecal steroid coprostanol. Tracing these three contaminants, he develops a model for contaminant transport through the estuary. The PCBs in this system appear to be associated primarily with the riverine–estuarine sediments and apparently do not flush out of the system onto the

TABLE 2. Permit quantities in 10^4 metric tonnes (t) of ocean-dumped wastes to the North Atlantic Ocean for 1979 from IMCO-LDC records.

Waste and country	Quantity
Sewage sludges	
Federal Republic of Germany	29
Ireland	10
United Kingdom	928
United States	688
Total	1 655
Industrial wastes	
Belgium	81.8
Denmark	3.4
France	476.6
Federal Republic of Germany	75
Ireland	3.6
Spain	52.5
United Kingdom	108.5
United States	406.2
Total	2 058.8
Dredged materials	
Belgium	3 048
Canada	900
France	143
Netherlands	407
United Kingdom	3 310
United States	1 635
Total	9 443
Coal wastes	
Spain	3.6
United Kingdom	228
Total	231.6
Fish wastes (Offal)	
Canada	0.68
Total	0.7
Solid wastes	
Canada	95
United States (construction debris)	79.2
Total	174.2
Radioactive wastes	
Belgium Netherlands Switzerland (beta + gamma = 836.9 Ci, tritium = 1249 Ci) (1 Ci = 37 GBq)	0.34
United Kingdom (beta + gamma = 40 089 Ci, tritium = 40 991 Ci)	0.20
Total	0.54
Grand total	13 533.84

adjacent shelf. These contaminants originate from an upriver industrial source but have become associated with the more downstream fine sediments of the estuary, where they are resuspended back into the estuarine water column.

The PAH load, not coprostanol, is linked to this redistribution of PCB. PAH concentrations in the harbor are relatively low (1–34 ng/L) and increase only during the flood, suggesting importation of PAHs from offshore or shelf sources. The source there, going by analytical characterization, is the PAH-rich sewage sludge, estimated to be 85–90% petroleum PAH. In contrast, the dredge spoils apparently represent largely a pyrogenic PAH source. Coprostanol movement is quite independent of both PCB and PAH, being found primarily in the surface waters of the estuary, with net transport out of the harbor onto the shelf.

The results demonstrated the tight coupling, through a number of compartments and pathways, between the riverine–estuarine environment and the shelf–offshore system, besides underlining the fact that different organic constituents have different sources and follow differing oceanographic and physical processes. One common thread, however, is the role of resuspended material in this transport. Thus, in Boehm's study, PCBs within the harbor apparently derive from resuspended harbor–estuarine sediments, while offshore the landward transport (during the flood) of PAHs apparently comes from resuspended sewage sludge dumped there.

The latter study and others in these proceedings emphasize the need for longer term sampling and for analytical studies over more extended or seasonal time periods. This would give both depth and breadth to the data, which so far have been obtained largely from single-station, single-sample geochemical–oceanographic "snapshots" (Boehm, this issue).

SESSION IV

Organic Synthetics

CO-CHAIRMEN

R. POCKLINGTON

Department of Fisheries and Oceans, Ocean and Aquatic Surveys, Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

AND KARSTEN PALMORK

Institute of Marine Research, Bergen N-5011, Norway

Accumulation of Cadmium and Polychlorinated Biphenyls by *Mytilus edulis* Transplanted from Pristine Water into Pollution Gradients[1]

W. C. DE KOCK[2]

Division of Technology for Society, Netherlands Organization for Applied Scientific Research (TNO), Delft, The Netherlands

DE KOCK, W. C. 1983. Accumulation of cadmium and polychlorinated biphenyls by *Mytilus edulis* transplanted from pristine water into pollution gradients. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 282–294.

Monitoring of bioavailable Cd and polychlorinated biphenyls (PCB) is technically feasible by transplanting mussels, *Mytilus edulis*, from a population with low contaminant levels into polluted waters elsewhere. This procedure improves resolution power between sites of investigation by minimizing population variance at the start of exposure experiments. In the current investigation, random samples (100 animals each) of similar-sized individuals (length class 4.0–5.0 cm) derived from a sublittoral Atlantic stock (western Ireland) were simultaneously exposed to selected locations in Dutch estuarine and marine waters. Although approximately equal yearly amounts of Cd (~50 t) reach the sea by way of the Scheldt and the Rhine–Meuse systems, accumulated Cd levels in *M. edulis* in the eastern part of the western Scheldt Estuary were clearly elevated after 60 d of exposure, whereas levels in mussels under Rhine–Meuse influence were not greatly enhanced. The literature suggests that this is partly due to different geochemical processes. Cadmium accumulation in *M. edulis* is a slow process in the field, and plateau levels are not reached after 60 d. Polychlorinated biphenyls probably reach plateau values within 2–3 mo. The data show clear bioavailable PCB gradients as a result of fluvial input into Dutch coastal waters both by the Scheldt and the Rhine–Meuse systems. Contrary to data for Cd, a conservative estuarine mixing behavior is suggested. Also unlike data for Cd, winter levels in *M. edulis* were higher by a factor of 2 as compared with summer values, both on the basis of ash-free dry weights and total lipids. Offshore PCB concentrations in transplanted mussels remained low but after 60 d were elevated above initial Atlantic levels.

DE KOCK, W. C. 1983. Accumulation of cadmium and polychlorinated biphenyls by *Mytilus edulis* transplanted from pristine water into pollution gradients. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 282–294.

Il est techniquement faisable de suivre le Cd et les BPC biologiquement utilisables en transplantant des moules bleues, *Mytilus edulis*, d'une population à bas niveau de contamination vers un endroit où les eaux sont polluées. On peut ainsi améliorer le pouvoir de résolution entre sites d'investigation en minimisant, dès le début de l'expérience, la variance de population. Dans la présente étude, des échantillons aléatoires (de 100 animaux) de moules de même taille (classe de longueur de 4,0–5,0 cm) provenant d'un stock sublittoral atlantique (Irlande occidentale) furent exposés simultanément en des endroits choisis dans des eaux estuariennes et marines hollandaises. Bien que des quantités à peu près égales de Cd (~50 t) soient déversées annuellement dans la mer par le Scheldt et le réseau Rhin–Meuse, les niveaux de Cd accumulé par *M. edulis* dans la partie orientale de l'estuaire du Scheldt occidental se sont nettement élevés après exposition de 60 jours, tandis que les niveaux dans les moules soumises à l'influence du réseau Rhin–Meuse n'ont pas varié pour la peine. Les données publiées laissent supposer que ceci est dû en partie à des processus géochimiques différents. L'accumulation de Cd chez *M. edulis* est un processus lent sur le terrain, et des plateaux ne sont pas atteints après 60 jours. Les BPC, par ailleurs, atteignent probablement un plateau en moins de 2–3 mo. Les données montrent de clairs gradients de BPC biologiquement utilisables à la suite des apports fluviaux dans les eaux côtières de Hollande, provenant à la fois du Scheldt et du réseau Rhin–Meuse. Il y aurait, contrairement au Cd, un mélange estuarien conservateur. Contrairement au Cd également, les niveaux chez

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Present address: Laboratory for Applied Marine Research (TNO), P.O. Box 57, 1780 AB Den Helder, The Netherlands.

Printed in Canada (J6869)
Imprimé au Canada (J6869)

M. edulis en hiver sont supérieurs d'un facteur 2 aux valeurs estivales, tant sur la base de poids sec sans les cendres que sur celle des lipides totaux. Les concentrations de BPC au large chez des moules transplantées demeurent faibles, mais, après 60 jours, elles dépassent les niveaux initiaux de l'Atlantique.

Received March 19, 1982
Accepted January 25, 1983

Reçu le 19 mars 1982
Accepté le 25 janvier 1983

COASTAL marine ecosystems in the Netherlands are susceptible to environmental damage by the anthropogenic input of toxic heavy metals and halogenated hydrocarbons, among which the nonessential element Cd and the xenobiotic polychlorinated biphenyls (PCB) have been recognized as potential hazardous substances (e.g. Goldberg 1976). Some earlier case studies have already demonstrated the importance of a marine pollutant transport mechanism along the Dutch coastline (Cu: Roskam 1965; chlorinated hydrocarbons: Koeman and van Genderen 1972) and illustrate the need for reliable monitoring systems.

Background levels of Cd and PCB encountered in offshore waters of the Southern Bight (50–100 km off the Dutch shoreline), which include input by precipitation following atmospheric transport to the North Sea (Cd: Cambray et al. 1979; PCB: Dawson and Riley 1977), are not highly elevated. Dissolved Cd values here amount to about 0.1 $\mu g \cdot L^{-1}$ (Duinker and Nolting 1977; lower values of Dutton et al. 1973; Anonymous 1979), a level that is not much above mean oceanic levels reported in the literature (e.g. reviews of Phillips 1977; Coombs 1979). Furthermore, background values for dissolved PCB in the Southern Bight reported by Dawson and Riley (1977) and Duinker and Hillebrand (1979) range from 0.5 to 0.7 $ng \cdot L^{-1}$ (standard reference Aroclor 1254), which is comparable with the lowest values for the North Atlantic published by Harvey et al. (1974). Input of pollutants by international river systems (Rhine–Meuse and Scheldt), either directly or indirectly via the dumping of fine-grained dredged deposits from downstream river sections, must therefore be considered to be the principal concern in Dutch coastal areas. It should be noted that the input into marine waters is only part of the total fluvial pollutant transport. Estimates in Table 1 show that less than 50% of the Cd and PCB load carried towards the Rhine–Meuse Delta is reaching the North Sea. The remainder is mainly retained in downstream eutrophic freshwater basins, this being the combined result of particle sedimentation at low current velocities, adsorption onto suspended matter at increasing pH values (Cd), and accumulation by freshwater phytoplankton (Salomons and Mook 1980). These freshwater sinks (the Ysselmeer, created in 1932, and the Haringvliet, separated from the North Sea in 1970) developed behind man-made protective barriers during the 20th century. In contrast, transport of pollutants by the Scheldt into the western Scheldt Estuary is largely unmodified by civil engineering activities.

In 1979–80 a feasibility study was undertaken to develop a method for monitoring bioavailable pollutants in Dutch coastal waters. The spatial and temporal distribution of Cd and PCB was investigated by measurements of the actual bioaccumulation process along the gradient caused by fluvial input from the Scheldt, Rhine, and Meuse. The study focused on the experimental use of mussels, *Mytilus edulis*, which were transplanted from a sublittoral Atlantic culture stock to several exposure locations in Dutch marine territory. The filter-feeding genus *Mytilus* appears to fulfill the basic prerequisites of a monitoring organism, which are listed by Phillips (1977, 1980) and the genus has already been applied in extensive monitoring schemes (e.g. Goldberg et al. 1978; National Academy of Sciences 1980) for practical reasons, e.g. wide distribution, abundance, size, ease of collecting, long life span, euryhalinity, general stress tolerance, accumulation ability, and high concentration factors for several chemicals.

To avoid natural variability related to age or size (Boyden 1974, 1977) and vertical position on the shoreline (de Wolf 1975) various authors attempted to measure bioavailable pollutants by transplanting mussels, *M. edulis*, to pollution gradients. This has been done, for instance, with positive

TABLE 1. Fluvial transport by Rhine, Meuse, and Scheldt and input into the North Sea of Cd and PCB (estimates based on data by Salomons et al. 1981 and Duinker and Hillebrand 1979).

	Rhine	Meuse	Scheldt	Rhine	Meuse
Water discharge ($km^3 \cdot yr^{-1}$)	69.4	10.3	3.2	69.4	10.3
Mud transport (particle size <50 μm) (10^6 $t \cdot yr^{-1}$)	3.4	0.7	1.0	3.4	0.7
	Cd (1977–78)			*PCB (1974–76)*	
Particulate transport ($t \cdot yr^{-1}$)	77.8	18.7	55.6	12.3	1.2
Dissolved transport ($t \cdot yr^{-1}$)	95.2	3.3	1.6	7.6	0.2
Total transport ($t \cdot yr^{-1}$)	173	22	57.2	19.9	1.4
Input into marine waters ($t \cdot yr^{-1}$)	53		57.2	~9.5	
via Rotterdam Waterway into North Sea	25		—	} ~5.0	
via Haringvliet sluices into North Sea	16		—		
via Ysselmeer sluices into North Sea	4		—	?	
via dumping dredged material into North Sea	8		—	~4.5	
via Scheldt into western Scheldt Estuary	—		57.2	—	

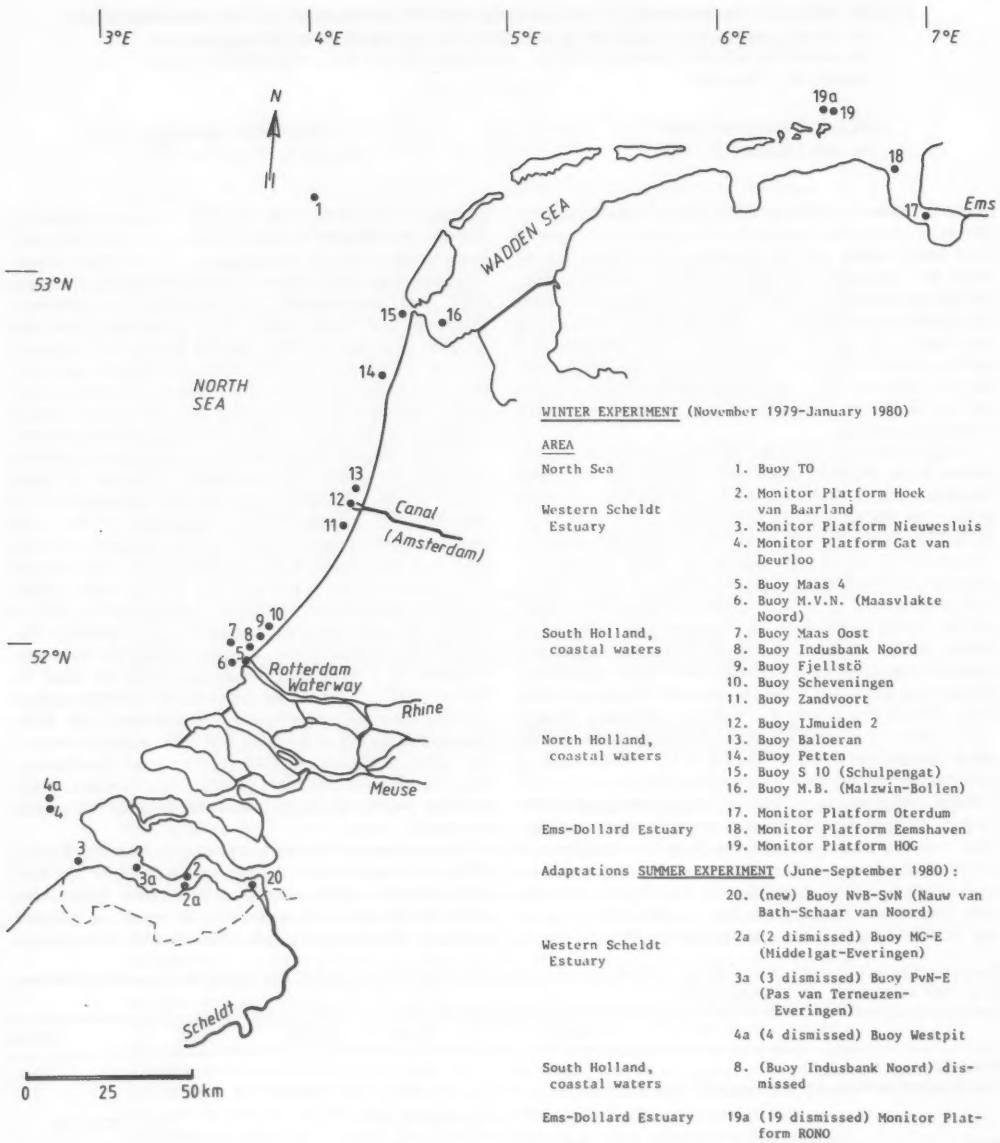

FIG. 1. Biomonitoring experiments with transplanted Atlantic mussels (*M. edulis*). Overview of exposure stations in the Netherlands, 1979–1980.

results for Hg, Cu, and Zn in the Netherlands (Hueck 1976), Hg in Scotland (Davies and Pirie 1978), Zn and Pb in northeast England (Simpson 1979), and various metals and hydrocarbons in Narragansett Bay, RI (Widdows et al. 1981). de Kock and Kuiper (1981) described how temporal variation of total Hg levels in *M. edulis* was decreased after changing from a "passive" monitoring scheme with intertidal mussels to an "active" biomonitoring approach in which large samples of

continuously submerged animals of a selected size class were transplanted from a relatively unpolluted site to the target area and suspended from buoys in cages. Such a transplantation technique may provide a useful approach because (1) it facilitates comparison between geographical locations by employing statistically similar groups of animals derived from a common stock, (2) the (chosen) period of exposure to the polluted environment is known, and (3) the investigator can select his monitoring locations independent of the natural occurrence of the monitoring species.

Materials and Methods

FIELDWORK

Two transplantation experiments were performed covering a winter period from November 1979 to January 1980 and a summer season from June to September 1980. Temperatures in Dutch coastal waters ranged from approximately 4 to 9°C in winter and from 15 to 19°C in summer.

Sublittoral mussels, *M. edulis*, 4.0–5.0 cm long were collected from a raft culture in Killary Harbour, an Atlantic inlet in western Ireland (temperature 13–14°C; salinity 30–35‰). Samples of 100 individuals each were randomly selected from this stock. The samples were immediately packed in polythene baskets (average mesh size approximately 1.5 cm^2) and resuspended on the raft at 2 to 6-m depth for a number of days prior to transportation. During this period, byssus attachment to the artificial substratum and fellow individuals occurred and clumps of mussels began to form. Transport was by air in moist polythene bags at low altitude. Upon arrival in the Netherlands, groups of six baskets each were immediately packed in epoxy-coated iron cages (20 kg; 60 × 55 × 30 cm) and suspended from nautical buoys or monitoring platforms at various exposure sites in coastal waters (Fig. 1). Exposure depth was 2–3 m below surface level, and care was taken to avoid collision damage due to continuous wave action. The logistics of this extensive operation were complicated, and several sea-going buoy tenders of the Dutch Lighthouse Service were involved. For technical reasons, some adaptations were required in the second experiment, especially in the western Scheldt Estuary. Samples were recollected after periods of 10, 25, and 60 d. From locations 5 (Buoy Maas 4) and 7 (Buoy Maas Oost), samples were also returned after 100 d in September 1980.

ANALYSIS

Following recollection, live samples were thoroughly rinsed with seawater at the exposure location to remove associated silt (pseudofaeces, faeces) and/or small fouling organisms (barnacles, hydroids). A purification period was considered to be of no special advantage, in agreement with Boalch et al. (1981), and samples were directly deep-frozen in polythene bags at −20°C in the laboratory. Subsequent treatment involved thawing at room temperature, severing the posterior adductor muscle, carefully draining interior water (20 min), removing all soft tissues with a titanium scalpel, and mixing with a homogenizer (Ultra-Turrax) modified with titanium rotor shaft and cutting blades. Homogenates thus consisted of the pooled tissues of approximately 100 individuals. Subsamples of homogenates were stored either in acid-cleaned beakers for metal analysis or acetone-cleaned beakers dried at 260°C and closed with aluminium foil for organic pollutant analysis. Subsamples of a standard homogenate kept at the laboratory were treated and analyzed the same way (metals: 1 per 10 samples; organics: 1 per 7 samples).

Cadmium was determined by AAS (Perkin Elmer 430 combined with HGA-500 graphite furnace and AS-1 automatic injection) using approximately 2 g of accurately weighed homogenate, digested in H_2SO_4 and H_2O_2, and diluted with distilled water.

PCB analysis involved several steps: (a) enzymatic destruction of the homogenate with pepsin (24 h, 37°C), (b) steam distillation and simultaneous extraction of PCB (and other chlorinated hydrocarbons) with *n*-hexane, (c) column chromatographic elution over silica gel (Merck No 7754, 60 reinst. 0.063–0.200 mm activated at 120°C and partly deactivated with 5% H_2O) of the PCB-containing low-polarity first fraction from the extract, using 8.5 mL *n*-hexane, (d) removal of hexane by azeotropic evaporation with CCl_4, (e) perchlorination of PCB to decachlorobiphenyl (DCB) with $SbCl_5$ (20 h) and extraction of DCB with *n*-hexane, and (f) gas chromatographic analysis with electron-capture detection involving comparison of peak heights in the chromatogram with Aroclor 1254 analytical standards following the complete procedure. Gas chromatographic characteristics were as follows: glass column 1 m, diameter 2 mm, stationary phase 1.5% OV − 17 + 1.95% OV − 210 on Chromosorb W-HP (80–100 mesh), injection volume 0.5 µL, detector linear ECD (type ^{63}Ni), column temperature 200°C, detector 300°C, injector 240°C, elution gas velocity approximately 25 $mL \cdot min^{-1}$.

Lipid content was determined gravimetrically after extraction of 5 g of homogenate with chloroform–methanol, 1:1, for 24 h, separation and filtration of the extract, and evaporation at 40°C under a N_2 atmosphere.

Separate subsamples were used to determine dry weight (after 16 h at 105°C) and ash content (after 4 h at 600°C). This was done to express analytical results on an ash-free dry weight (a.f.d.w.) basis. Using merely a dry weight basis may introduce bias due to salinity variations in the tissue fluids of *M. edulis*, especially in estuarine areas. *Mytilus edulis* is highly isotonic with its external environment (Potts 1954), and its ash is composed largely (>75%) of inorganic sea salt components, as has been found by analysis of major cations and anions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}). Furthermore, significant linear correlations between ash content and water content have been found experimentally by the author to shift after transfer of test animal samples to different salinities.

MONITORING METHOD

Differences in mean pollutant levels between populations of *M. edulis* are usually investigated in relation to variables such as season or geographical location within a gradient. To resolve such differences by biomonitoring, maximal effort is required to minimize population variance. This has been done using animals of a single length class from the same

TABLE 2. Cadmium in *M. edulis* transplanted from Atlantic waters to coastal stations in the Net
grams per gram ash-free dry weight total soft tissues).

Station[a]	Area	November 1979–January 1980 (winter), exposure period (d)[b] 10		25		60	
1	North Sea, offshore	0.85		0.53		0.72	
20		—		—		—	
2		1.02		1.68		3.07	
2a		—		—		—	
3	Western Scheldt Estuary	Lost		Lost		0.89	
3a		—		—		—	
4		0.56		0.53		0.69	
4a		—		—		—	
	Area mean (SD)	0.79	(0.33)	1.10	(0.81)	1.55	(1.
5		0.76		0.98		1.01	
6		1.07		1.55		1.02	
7		0.71		0.95		0.88	
8	South Holland, coastal waters	0.83		1.02		0.85	
9		0.76		1.14		0.89	
10		0.85		1.06		1.23	
11		0.71		1.09		0.89	
	Area mean (SD)	0.81	(0.13)	1.11	(0.20)	0.97	(0.
12		0.70		0.92		0.82	
13		1.29		1.27		Lost	
14	North Holland, coastal waters	0.66		1.03		1.18	
15		0.75		1.24		1.01	
16		0.46		0.84		0.92	
	Area mean (SD)	0.77	(0.31)	1.06	(0.19)	0.98	(0.
17		0.52		0.30		0.61	
18		0.35		0.53		0.70	
19	Ems–Dollard Estuary	0.44		0.46		0.74	
19a		—		—		—	
	Area mean (SD)	0.44	(0.08)	0.43	(0.12)	0.68	(0.

[a]See Fig. 1.
[b]Initial Cd concentration 0.65 (SD = 0.13, n = 4).
[c]Initial Cd concentration 0.93 (SD = 0.04, n = 5).

n the Netherlands (length class 4.0–5.0 cm, sample size 100 individuals, concentrations in micro-

	June 1980–September 1980 (summer), exposure period (d)[c]								Local sublittoral samples
60	10		25		60		100		
0.72	0.90		1.07		0.67		—		1.37
—	1.91		3.24		5.80		—		—
3.07	—		—		—		—		—
—	2.10		1.90		6.53		—		—
0.89	—		—		—		—		—
—	1.25		1.04		3.59		—		—
0.69	—		—		—		—		—
—	0.64		0.46		0.66		—		—
1.55 (1.32)	1.48	(0.67)	1.66	(1.21)	4.15	(2.64)	—		—
1.01	1.39		1.26		1.67		1.72		—
1.02	1.36		0.90		1.69		—		—
0.88	1.28		0.93		1.20		1.13		—
0.85	—		—		—		—		—
0.89	1.07		0.82		Lost		—		1.65
1.23	1.27		0.90		Lost		—		1.62
0.89	0.75		0.86		1.20		—		1.60
0.97 (0.13)	1.19	(0.24)	0.95	(0.16)	1.44	(0.28)	1.43	(0.42)	—
0.82	0.71		0.74		0.83		—		—
Lost	0.65		0.71		Lost		—		—
1.18	0.61		0.52		1.09		—		—
1.01	0.64		0.54		0.80		—		—
0.92	0.65		0.54		0.59		—		—
0.98 (0.15)	0.65	(0.04)	0.61	(0.11)	0.83	(0.21)	—		—
0.61	0.83		0.94		1.24		—		—
0.70	0.68		0.59		0.85		—		—
0.74	—		—		—		—		—
—	0.72		0.64		Lost		—		—
0.68 (0.07)	0.74	(0.08)	0.72	(0.19)	1.05	(0.28)	—		—

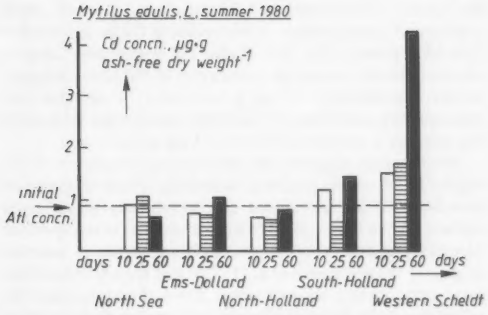

FIG. 2. Cadmium concentrations in Atlantic *M. edulis* samples (4.0–5.0 cm, 100 individuals pooled per sample) transplanted to marine waters of the Netherlands. Means are given for five subareas after 10, 25, and 60 d of exposure, summer, June–September 1980 (ref. Table 2).

nonspawning and nonpolluted stock and by dividing these animals randomly between experimental samples of 100 mussels each. This design should eliminate a substantial part of the variability between samples at the start of the transplantation experiments (de Kock and Kuiper 1981). Gordon et al. (1980) showed with *Mytilus californianus*, for a number of trace metals, in what way the required number of analyses of individual animals changes with the percentage difference between population means that can be detected. Resolution is much improved when the number of individual analyses used for one sample increases up to a sample size of about 30 individuals; but clearly, the analytical load restricts the usefulness of this approach (certainly so for gas chromatographic analysis of organic pollutants). For Cd in *M. californianus* it is mentioned (Gordon et al. 1980) that 60–80 individual analyses are required to detect a 20% difference between means by *t*-test.

The advantage of pooling many individual organisms into a single sample is that a good estimate of the mean concentration of a pollutant in a population should become available without unmanageable analytical programs. Thus, with *M. edulis*, de Wolf (1975) observed that pooled samples of at least 60 individuals in each 0.5-cm length class were required to obtain a measured Hg concentration within ±10% of the population mean with a probability of 95%, and Martin and Phelps (1979) plotted the relation between number of pooled *M. edulis* samples and number of individuals per pool giving 90% certainty of detecting differences between means of Cu concentrations with $P = 0.05$ at various degrees of resolution (5, 10, 20, 50, or 100%) using a *t*-test. Extrapolation of these plots indicates that when a pool contains 100 individuals, only very few (possibly 1) samples are required even for detecting a 5% difference between means. Unfortunately, such plots are not available for PCB and Cd in the present study. It is assumed, however, that 100 pooled and randomly selected individuals per sample should constitute a fairly reliable sample size. In this case, resolution power will probably finally be limited by analytical reliability. In the present study, variation coefficients were determined for Cd and PCB values in

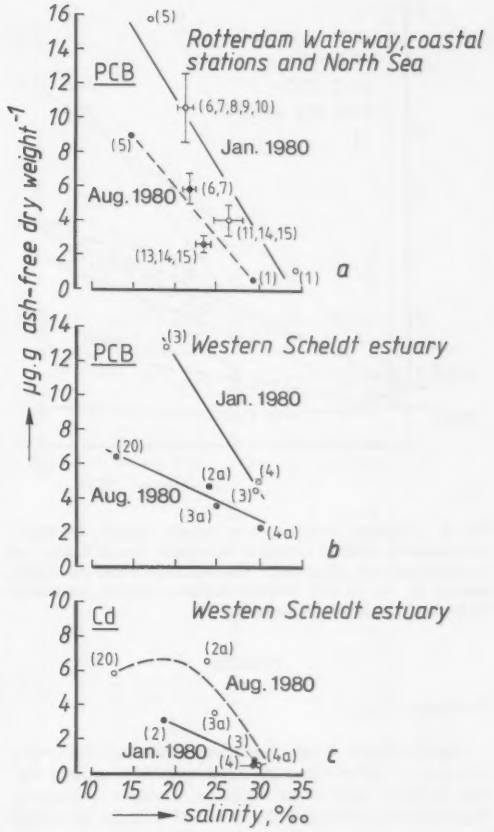

FIG. 3. Plots of PCB and Cd in *M. edulis* against salinities of tissue homogenates. Transplanted Atlantic samples recollected after 60 d. Station Nos. indicated in parentheses (see Fig. 1). Station 5 is in the Rhine–Meuse estuarine mixing zone; combined stations 6–10 (area South Holland) and 11–15 (area North Holland) are in open coastal waters. Within-area variations are represented by horizontal and vertical bars (±1 SD). Stations 12 and 16 are omitted because of local salinity disturbances. Linear correlations (significant at $P = 0.05$) have been found for PCB in the Rhine–Meuse sphere of influence (Fig. 3a) and the western Scheldt Estuary (Fig. 3b). Cadmium in the western Scheldt Estuary shows a nonconservative relationship (August 1980, Fig. 3c).

a standard homogenate of *M. edulis* tissue, kept deep-frozen in the laboratory and routinely analyzed with summer and winter field samples. Variation in PCB analysis was larger (coefficient of variation = 30–42%) than in Cd measurements (coefficient of variation = 7.3–9.0%). At $P = 0.05$ and assuming normality, real Cd and PCB values will deviate no more than 2 standard deviations from the measured concentrations (i.e. 14.6–18% for Cd and 60–84% for PCB).

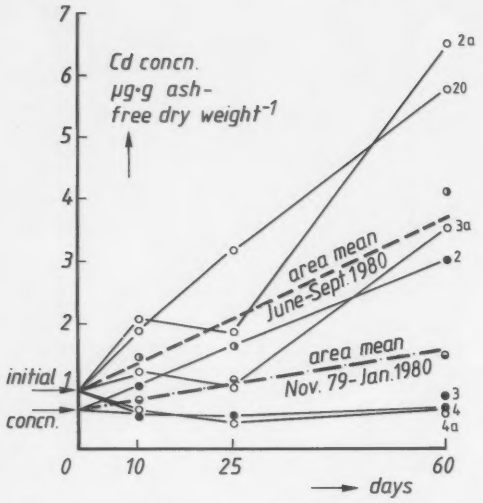

FIG. 4. Cadmium accumulation in Atlantic mussels, *M. edulis*, transplanted to different stations in the western Scheldt Estuary and recollected after 10, 25, and 60 d. Stations 2, 3, 4, winter experiment; stations 2a, 3a, 4a, 20, adapted locations, summer experiment. Arrows indicate initial concentrations.

Results

CADMIUM (TABLE 2)

Initial Atlantic levels were low: 0.65 and 0.93 $\mu g \cdot g$ $(a.f.d.w.)^{-1}$ in November 1979 and June 1980, respectively. This is below many of the values for *M. edulis* reviewed by Phillips (1977, 1980) or "mussel watch" values in the United States reported by Goldberg et al. (1978) and in reasonable agreement with the low values reported by Cossa et al. (1980) for the western Atlantic (Gulf of St. Lawrence).

Although *M. edulis* acts as a good indicator for Cd pollution (Bryan 1980), accumulation was poor in the area where influence by input from the Rhine–Meuse system is expected to be the greatest (coastal waters of South Holland). Cadmium concentrations in mussel tissue did not increase by more than a factor of 1.5 after 60 d of exposure in this area, and differences generated between the results here and those of the offshore North Sea are small (Fig. 2). This distribution pattern did not show appreciable interseasonal changes, nor did absolute concentration values. The observations of Jackim et al. (1977), which show Cd uptake to be independent of temperature, may have some relevance here. It is probable that decreased bioavailability of dissolved Cd species (Marquenie 1981) and removal from the water phase by transition to a particulate state in downstream freshwater reservoirs or the early estuarine mixing zone efficiently reduce the ambient concentration of bioavailable Cd in the coastal zone. Values for the Ems–Dollard Estuary remained as low as those for the offshore North Sea and hardly deviated from the Atlantic values mentioned. The results do, however, show a clear pollution gradient of bioavailable Cd in the western Scheldt Estuary (Fig. 3c). Cadmium levels were already shown to be elevated in the eastern part of this area during the winter experiment (3.07 $\mu g \cdot g$ $(a.f.d.w.)^{-1}$), and this was subsequently confirmed by adjusting monitoring stations in the summer experiment (5.80–6.53 $\mu g \cdot g$ $(a.f.d.w.)^{-1}$).

The literature suggests that physiological regulation of Cd uptake by *M. edulis* is absent, indicating simple diffusion of dissolved Cd species across cell membranes at the body surface. When Cd supplied from food sources is incorporated (Janssen and Scholz 1979), overall linear uptake is assumed (e.g. von Westernhagen et al. 1978), and known elimination rates are taken into account, about 300 d of accumulation are calculated to be required to reach equilibrium levels (Scholz 1980). The present field transplantation data also show Cd accumulation in *M. edulis* to be a slow process (Fig. 4). Cadmium concentrations of some samples, locally settled and grown on the buoy stations 1, 9, 10, and 11 (South Holland coastal waters, Table 2), support this observation. Age of these samples should be about 1 yr, and Cd concentrations were higher than those of the transplanted samples after 25 or 60 d. Also, two transplanted samples recollected after 100 d (stations 5 and 7) indicated that equilibration is an exceedingly slow process (and perhaps not even possible if excretory ability should decrease with age). In view of the long equilibration period mentioned and the nearly linear accumulation pattern found during the first 60 d, the eastern part of the western Scheldt area should be considered to be substantially polluted with bioavailable Cd. This agrees with data of Duinker and Nolting (1977), who reported the highest marine concentrations for dissolved Cd in the Netherlands form the western Scheldt area (0.6 $\mu g \cdot L^{-1}$).

PCB (TABLES 3 AND 4)

Initial Atlantic levels were unexpectedly high in November 1979 (0.86 $\mu g \cdot g$ $(a.f.d.w.)^{-1}$). This value might be due to analytical errors because lower values were found after 10 d of exposure in the North Sea (station 1) and the Ems–Dollard Estuary (stations 17–19). Initial Atlantic values found in June 1980 were low (0.09 $\mu g \cdot g$ $(a.f.d.w.)^{-1}$) and well in the range of lower concentrations reported for *M. edulis* from Atlantic stations in the United States (Goldberg et al. 1978). Clear accumulation patterns of PCB were found in Dutch coastal waters for both the winter and summer exposure periods. The average accumulation curves constructed for various subareas (Fig. 5) suggest that net uptake of PCB is a slow process: plateau levels were not reached after 60 d in the winter, and up to 100 d were required in the summer of 1980. PCB concentrations gradually decrease in the northerly direction along the Dutch coast, presumably according to a conservative mixing model (Fig. 3a). In the entrance to the Wadden Sea (station 15) and in the western Wadden Sea (station 16) concentrations were found that are still elevated as compared with Atlantic levels. These values expressed on a lipid base (Table 4) as Aroclor 1254 were somewhat lower (6.6–9.1 $\mu g \cdot g^{-1}$) after 60 d of accumulation at station 16 than the general values formerly reported by Hagel and Tuinstra (1978) for commercial *M. edulis* from the Wadden

TABLE 3. PCB in *M. edulis* (analyzed as decachlorobiphenyl) transplanted from Atlantic waters t
100 individuals, concentrations in micrograms per gram ash-free dry weight total soft tissues).

Station[a]	Area	November 1979–January 1980 (winter), exposure period (d)[b] 10		25		60		
1	North Sea, offshore	0.21		0.27		1.21		0.
20		—		—		—		3.
2		1.64		1.53		12.82		-
2a		—		—		—		2.
3	Western Scheldt Estuary	Lost		Lost		4.46		-
3a		—		—		—		1.
4		0.57		7.48		4.98		-
4a		—		—		—		0.
	Area mean (SD)	1.11	(0.76)	4.51	(4.21)	7.42	(4.68)	1.
5		1.94		6.68		15.79		2.
6		3.18		5.40		12.13		2.
7		1.72		na		9.66		2.
8	South Holland, coastal waters	3.40		1.61		10.18		-
9		1.12		5.25		13.01		2.
10		3.89		5.43		7.97		2.
11		1.43		2.42		4.40		1.
	Area mean (SD)	2.38	(1.09)	4.47	(1.98)	10.45	(3.68)	2.
12		0.99		3.80		14.28		1.
13		1.19		2.24		Lost		1.
14	North Holland, coastal waters	1.31		2.09		4.77		1.
15		0.63		1.05		3.02		2.
16		0.28		1.22		2.30		0.
	Area mean (SD)	0.88	(0.42)	2.08	(1.09)	6.09	(5.56)	1.
17		0.21		0.52		1.42		0.
18	Ems–Dollard Estuary	0.32		0.58		1.46		0.
19		0.17		0.96		2.12		-
19a		—		—		—		0.
	Area mean (SD)	0.23	(0.08)	0.69	(0.24)	1.67	(0.39)	0.

[a]See Fig. 1.
[b]Initial concentration in Atlantic samples 0.86 (SD = 0.81, n = 5); na, not analyzed.
[c]Initial concentration in Atlantic samples 0.09 (SD = 0.13, n = 5); na, not analyzed.

waters to coastal stations in the Netherlands (length class 4.0–5.0 cm, sample size

	June 1980–September 1980 (summer), exposure period (d)[c]								Local sublittoral samples
	10		25		60		100		
	0.50		0.17		0.66		—		0.95
	3.17		2.96		6.40		—		—
	—		—		—		—		—
	2.51		2.21		4.69		—		—
	—		—		—		—		—
	1.18		0.90		3.57		—		—
	—		—		—		—		—
	0.67		na		2.25		—		—
4.68)	1.88	(1.16)	2.02	(1.04)	4.23	(1.76)	—		—
	2.97		2.88		8.97		9.02		—
	2.34		2.53		6.50		—		—
	2.72		3.84		5.24		3.47		—
	—		—		—		—		—
	2.67		2.62		Lost		—		1.93
	2.79		5.28		Lost		—		5.13
	1.72		2.21		2.38		—		1.95
3.68)	2.54	(0.45)	3.23	(1.15)	5.77	(2.74)	6.25	(3.92)	—
	1.11		2.98		2.41		—		—
	1.32		2.11		Lost		—		—
	1.03		0.79		3.19		—		—
	2.12		0.87		2.43		—		—
	0.66		0.72		1.67		—		—
5.56)	1.25	(0.54)	1.49	(1.01)	2.43	(0.62)	—		—
	0.67		2.95		2.09		—		—
	0.28		0.18		1.36		—		—
	—		—		—		—		—
	0.38		0.35		Lost		—		—
0.39)	0.44	(0.20)	1.16	(1.55)	1.73	(0.52)	—		—

TABLE 4. PCB in *M. edulis* (analyzed as decachlorobiphenyl) transplanted from Atlantic
size 100 individuals, concentrations in micrograms per gram on the basis of total lipids,

Station[a]	Area	November 1979–January 1980 (winter), exposure period (d)[b] 10		25		60
1	North Sea, offshore	1.4		1.7		5.(
20		—		—		—
2		9.6		9.6		70.(
2a		—		—		—
3	Western Scheldt Estuary	Lost		Lost		35.5
3a		—		—		—
4		3.8		40.3		32.8
4a		—		—		—
	Area mean (SD)	6.7	(4.1)	25.0	(21.7)	46.
5		12.7		45.1		128.3
6		17.2		41.8		72.5
7		7.3		na		55.4
8	South Holland, coastal waters	15.1		10.4		68.7
9		5.4		40.3		81.9
10		15.8		42.9		42.(
11		8.6		18.5		26.5
	Area mean (SD)	11.7	(4.6)	33.2	(14.8)	68.(
12		4.0		28.4		110.1
13		8.8		15.6		Lost
14	North Holland, coastal waters	13.7		10.0		42.9
15		4.3		4.6		20.(
16		2.4		9.2		14.4
	Area mean (SD)	6.6	(4.6)	13.6	(9.2)	47.(
17		1.3		2.1		8.2
18	Ems–Dollard Estuary	2.3		3.7		15.7
19		1.6		5.1		20.4
19a		—		—		—
	Area mean (SD)	1.7	(0.5)	3.6	(0.2)	14.8

[a]See Fig. 1.
[b]Initial concentration in Atlantic samples 4.9; na, not analyzed.
[c]Initial concentration in Atlantic samples 0.6; na, not analyzed.

Atlantic waters to coastal stations in the Netherlands (length class 4.0–5.0 cm, sample
tal lipids, soft tissues).

– nter), (d)[b]		June 1980– September 1980 (summer), exposure period (d)[c]							
60		10		25		60		100	
5.6		3.3		0.7		7.2		—	
—		14.1		13.9		29.5		—	
70.0		—		—		—		—	
—		9.4		18.3		30.3		—	
35.5		—		—		—		—	
—		4.6		8.4		19.7		—	
32.8		—		—		—		—	
—		2.2		na		11.8		—	
46.1	(20.7)	7.6	(5.3)	13.5	(5.0)	22.8	(8.8)	—	
128.3		12.0		13.9		47.8		49.0	
72.8		13.1		12.6		29.4		—	
55.4		11.9		23.8		32.3		20.0	
68.7		—		—		—		—	
81.9		14.0		13.4		Lost		—	
42.6		14.0		29.8		Lost		—	
26.5		8.4		10.6		11.3		—	
68.0	(32.6)	12.2	(2.1)	17.4	(7.6)	17.4	(7.6)		
110.1		5.0		13.4		15.1		—	
Lost		5.5		10.7		Lost		—	
42.9		4.9		4.4		10.6		—	
20.6		9.2		3.7		14.6		—	
14.4		2.6		5.7		10.4		—	
47.0	(43.8)	5.4	(2.4)	7.6	(4.3)	12.7	(2.5)	—	
8.2		2.5		19.0		10.2		—	
15.7		1.1		1.2		7.9		—	
20.4		—		—		—		—	
—		2.9		1.6		Lost		—	
14.8	(6.2)	2.2	(0.9)	7.3	(10.2)	9.1	(1.6)	—	

Sea in 1972–76. Elevated levels are nevertheless important because PCB are suspected to cause reproductive failure of harbour seals (*Phoca vitulina*) in this area (Reijnders 1980, 1981). A gradient is also shown in the western Scheldt Estuary with a strong PCB accumulation in the eastern part, probably reflecting PCB input by the river Scheldt (Fig. 3b). Samples transplanted to the Ems–Dollard Estuary and the offshore North Sea showed relatively low PCB levels, but at 60 d of exposure these were still higher than initial values from western Ireland.

Discussion

Cadmium

Regarding Cd concentrations accumulated by *M. edulis* in the western Scheldt Estuary, comparable values are known from other places in Europe or east coast stations in the United States. For example, in Europe, Theede (1980) reported Cd concentrations from polluted Baltic waters ranging from 1–4 $\mu g \cdot g$ dry weight^{-1} (outer part of Kiel Bay, Germany) to 30 $\mu g \cdot g$ dry weight^{-1} (inner part of Kiel Fjord); Segar et al. (1971) found 5.1 $\mu g \cdot g$ dry weight^{-1} from the Solent (United Kingdom) and Stenner and Nickless (1974) found levels of 1.9–4.7 $\mu g \cdot g$ dry weight^{-1} (Skjerstadfjord) and 4.8–140 $\mu g \cdot g$ dry weight^{-1} (Hardangerfjord) in polluted Norwegian waters. At east coast stations in the United States such elevated levels have been reported by Goldberg et al. (1978) from New Haven, CT (6.2 $\mu g \cdot g$ dry weight^{-1}) and the New York area (4.2–4.7 $\mu g \cdot g$ dry weight^{-1}).

The difference noted between Cd concentrations reached in mussels transplanted to waters of the Rhine–Meuse Estuary and those observed in the eastern part of the western Scheldt Estuary is intriguing. With approximately equal yearly inputs (Table 1), a higher Cd buildup could be explained by longer residence times, but geochemical mechanisms might also be important. Whereas Duinker and Nolting (1977) mentioned removal of dissolved Cd species in the Rhine–Meuse Estuary, because concentrations of dissolved Cd at salinities of 0.4–35‰ are lower than expected with conservative mixing, Salomons et al. (1981) mentioned the reverse process for the western Scheldt Estuary, where transfer of particulate Cd to dissolved Cd species appears to take place. This could be a highly stimulating process for final uptake in *M. edulis*, as increased bioavailability of Cd would accompany it.

PCB

Clearly, fluvial output of the Rhine–Meuse system is reflected in PCB levels of *M. edulis* tissue after 60 d. Even when the analytical perchlorination effect is taken into account and results are expressed as Aroclor 1254 (63% of the values given in Tables 3 and 4), concentrations seawards of the river outflow (stations 5–10) range from 3.30–5.65 $\mu g \cdot g$ (a.f.d.w.)$^{-1}$ (summer) to 5.02–9.95 $\mu g \cdot g^{-1}$ (winter). Such high values have not been reported from the east coast of the United States but are known from highly industrialized areas on the west coast. Goldberg et al. (1978) reported PCB concentrations >1 $\mu g \cdot g$ dry weight^{-1} from San Diego Harbor (1.2–1.4 $\mu g \cdot g^{-1}$) and San Pedro Harbor (1.0–8.7 $\mu g \cdot g^{-1}$).

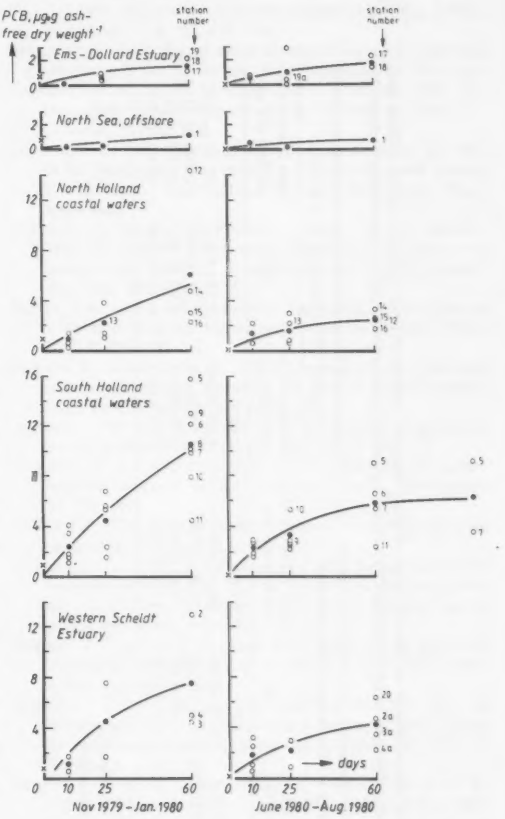

FIG. 5. PCB in *M. edulis* samples (4.0–5.0 cm, 100 individuals per sample) transplanted from Atlantic waters to various stations in Dutch coastal waters and the North Sea. Recollection after 10, 25, and 60 d. Results represent decachlorobiphenyl in soft tissues. *x* indicates initial concentrations (ref. Table 3). Mean concentrations per sampling date are used to draw accumulation patterns in five different subareas. Station Nos. refer to positions in Fig. 1.

All available PCB levels based on total lipids (x, Table 4) correlate significantly with PCB expressed on an ash-free dry weight base (y, Table 3). The correlation is given by $y = 0.27 + 0.14x$ for the winter series ($n = 53$, $r = 0.97$, $P < 0.005$) and $y = 0.13 + 0.18x$ ($n = 54$, $r = 0.97$, $P < 0.005$) for the summer series, showing that lipid content is a fairly constant percentage of ash-free dry weight. This suggests that lipid variability between samples is too small to affect PCB uptake patterns substantially, and that rather, the external environment is causing geographical differences in PCB levels in *M. edulis*. This might be confirmed by plots of PCB concentrations of the animals after 60 d against tissue-fluid salinity, which (because of isotony) expresses that of the

TABLE 5. Weight, growth, and lipid content of *M. edulis* transplanted from Atlantic waters (Killary Harbour, western Ireland) to Dutch coastal stations and recollected after 60 d (data combined for different subareas; within-area variation indicated by standard deviation (in parentheses); GF = growth factor relative to initial Atlantic samples).

		January 1980 (winter), 60-d exposure[b]			August 1980 (summer), 60-d exposure[c]		
Station[a]	Area	Ash-free dry wt individual (g)	GF	Total lipids (% of ash-free dry wt)	Ash-free dry wt individual (g)	GF	Total lipids (% of ash-free dry wt)
1	North Sea	0.56	0.77	21.69	0.90	2.05	9.24
2–4	Western Scheldt Estuary	0.69 (0.06)	0.94 (0.09)	16.87 (0.63)	0.68 (0.36)	1.55 (0.81)	18.56 (2.58)
5–11	Coast South Holland	0.72 (0.10)	0.99 (0.14)	16.89 (0.78)	1.04 (0.48)	2.35 (1.09)	20.64 (1.71)
12, 14–16	Coast North Holland	0.79 (0.07)	1.08 (0.10)	13.87 (1.81)	0.84 (0.30)	1.90 (0.69)	17.01 (9.81)
17–19	Ems–Dollard Estuary	0.68 (0.02)	0.93 (0.03)	12.68 (2.94)	0.41 (0.14)	0.93 (0.33)	18.83 (2.38)

[a]See Fig. 1.
[b]Initial Atlantic values: 0.73 g a.f.d.w. and 17.44% of total lipids.
[c]Initial Atlantic values: 0.44 g a.f.d.w. and 16.10% of total lipids.

external environment and which can be calculated by relating ash content to water content of the homogenates. These plots suggest general conservative linear relationships reflecting the fluvial origin of PCB in Dutch coastal waters (Fig. 3a and 3b). Such a conservative behavior implies that bioavailable PCB does not react drastically with the receiving marine environment (e.g. by deposition) within the residence time along the Dutch shore (several weeks) and that relatively significant amounts of PCB do not become available for *M. edulis* from bottom deposits or unexpected sources on the salinity gradient. Probably, only dissolved PCB and particulate PCB associated with the (re)suspended fine mud (e.g. dumping of polluted dredged material) have special relevance in these monitoring experiments with *M. edulis*. More detailed investigations should, however, clarify the situation.

A seasonal effect is also shown in Fig. 3. Contrary to what was found with Cd, winter PCB concentrations in *M. edulis* were higher than summer concentrations by a factor of approximately 2. It is not known if this reflects quantitative differences of abiotic environmental concentrations or is related to some biological factor. The seasonal effect is obviously not related to lipid concentrations because the latter do not show a comparable increase during winter and are even slightly higher in summer. However, mean growth rate observed in ash-free dry weight of the transplanted samples is substantially higher in summer (approximately $6\ mg \cdot d^{-1} \cdot mussel^{-1}$) than it is in winter (no growth), as is demonstrated by the growth factors in Table 5. This suggests a growth dilution factor to be important and that assimilation rates of PCB and utilized food supply (i.e. particulates >2 μm, nanoplankton, organic detritus) (Bayne 1976) are not interdependent, possibly pointing to the major role of a dissolved or very finely suspended PCB fraction for the accumulation observed and the uptake involved. Lower levels in *M. edulis* could also be explained by generally reduced ambient bioavailable PCB concentrations in the summer season, for which (apart from possible temporal changes in input into the North Sea) different hypothetical mechanisms could be held responsible (e.g. generally increased photochemical decomposition and increased biodegradation rates of less chlorinated isomers (Kalmaz and Kalmaz 1979) under summer conditions of light and temperature). Competition for dissolved PCB between *M. edulis* and summer populations of phytoplankton and zooplankton organisms in Dutch coastal waters could be another mechanism.

Fate of Cd and PCB in Dutch Coastal Waters

Dissolved and suspended pollutants of fluvial origin reaching the North Sea in the zone of coastal continental water along the Dutch shore are subject to a north-going residual current with a mean velocity of approximately $5\ cm \cdot s^{-1}$ (Otto 1964; van Bennekom et al. 1974). Part of the suspended fraction consists of resuspended particles joining coastal waters through dumping of dredged spoil from fairways and harbors in the Rotterdam area (Terwindt 1978). This spoil contains at least 50% mud (particle size <50 μm) and contributes considerably to the mud budget of the North Sea. Mechanisms that govern the subsequent fate of pollutants are only partly understood because of the complex set of environ-

mental variables acting upon them. However, as already mentioned, clear evidence is available that the residual current carries pollutants towards the Dutch Wadden Sea, thus possibly reducing the value of this important estuarine ecosystem as a natural sanctuary and a nursery ground for commercial fish. In this area, pollution is considered to be one of the main management problems (Wolff and Zijlstra 1980). Postma (1961) has already described the process of net transport of living and dead suspended material from the North Sea into the Wadden Sea, and Salomons and de Groot (1978) showed a gradual increase of heavy metal concentrations in sediments of the area, notwithstanding the fact that mobilization processes may occur in the upper layers of the sediments, which probably lead to a reduction of the net metal accumulation (Duinker et al. 1974). Exchange of metal-enriched interstitial water and overlying water by bioturbation and tidal action could result in a net transport of soluble and nonsettling colloidal fractions back to the North Sea. This would be analogous to the fate of mineralized dissolved phosphorus compounds in the area, as described by de Jonge and Postma (1974).

The present study suggests that, notwithstanding gradually increasing Cd levels in estuarine deposits downstream of the Rhine−Meuse system, the immediate influence of fluvial Cd input into the North Sea is not manifest in highly elevated levels of dissolved or suspended Cd species that become bioavailable for *M. edulis*. Only the eastern part of the western Scheldt is identified as a strongly polluted area, but the gradient is steep and the influence of the Scheldt as a fluvial source cannot be detected with *M. edulis* in the North Sea directly outside the estuary. The marine PCB distribution appears to be of a more serious nature. Accumulation of these compounds by *M. edulis* is highly efficient in Dutch coastal waters, and the coastal transport mechanism mentioned is confirmed by the data. Accumulated background levels in the offshore North Sea after 60 d were already higher by a factor of 1.5−7 as compared with Atlantic levels, concentrations outside the western Scheldt Estuary were clearly elevated, and the gradient caused by fluvial input of the Rhine−Meuse system extended into the Wadden Sea.

Acknowledgments

Thanks are due to Dr R. Dortland (Department of Transport and Public Works, North Sea Directorate), who stimulated publication of the data, to Pat Dinneen and John O'Carroll, who graciously cooperated in the collection of Atlantic mussel samples, to the enthusiastic team of the TNO Laboratory for Applied Marine Research in Den Helder, to those colleagues of the Analytical Chemistry Department MT-TNO in Delft, who participated in the project, and to various buoy tender crews of the Dutch Lighthouse Service.

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Calculation of Diffusion Resistances Controlling Volatilization Rates of Organic Contaminants from Water[1]

DONALD MACKAY,[2] WAN YING SHIU, AND EVA CHAU

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont. M5S 1A4

MACKAY, D., W. Y. SHIU, AND E. CHAU. 1983. Calculation of diffusion resistances controlling volatilization rates of organic contaminants from water. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 295–303.

A theoretical analysis is presented describing the rates of volatilization (and thus half-lives) of organic compounds from solution in surface waters, which is a reformulation of the existing "two-resistance" approach. It is extended to treat the more complex situation of volatilization from water in which the solute is also present in dispersed oil particles or in sorbed form and experiences a dissolution resistance which may prolong the volatilization half-life. We suggest that the separate calculation of half-lives (1) for volatilization from solution and from dispersion and (2) for dissolution assists the elucidation of the dominant rate-controlling processes. Satisfactory agreement is obtained between predicted concentration decay behaviour and data obtained in exploratory laboratory experiments and under dispersed oil slicks at sea.

MACKAY, D., W. Y. SHIU, AND E. CHAU. 1983. Calculation of diffusion resistances controlling volatilization rates of organic contaminants from water. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 295–303.

L'article qui suit contient une analyse théorique des taux de volatilisation de composés organiques d'une solution dans les eaux de surface, et qui est une reformulation de l'approche existante des "deux résistances." Nous élargissons l'analyse pour traiter la situation plus complexe de la volatilisation de l'eau dans laquelle le produit dissous est également présent dans les particules de pétrole dispersées ou sous forme sorbée et rencontre ainsi une résistance à la dissolution susceptible de prolonger la demi-vie de volatilisation. Nous avançons l'hypothèse qu'un calcul séparé des demi-vies (1) de volatilisation par solution et dispersion et (2) de dissolution aide à mieux comprendre le rôle dominant des processus de régulation. Nous obtenons un assez bon accord entre l'affaiblissement de concentration prédit et les données résultant d'essais exploratoires en laboratoire et sous des nappes de pétrole dispersées en mer.

Received March 19, 1982
Accepted October 13, 1982

Reçu le 19 mars 1982
Accepté le 13 octobre 1982

FOR many organic contaminants, such as petroleum hydrocarbons or organohalides, volatilization may be an important process controlling their water column concentrations and hence their toxicity. It is thus useful to have the capability of estimating the volatilization rate or a "half-life" in the water column, because these quantities can be compared with other rate data for competing processes such as biodegradation or photolysis.

Liss and Slater (1974) first presented a framework for calculating volatilization from solution using the "two-resistance" approach. In this work, we derive their equations in a modified form, which is then extended to treat, theoretically, the more complex situations in which a contaminant is present in a dispersed solid or liquid phase such as oil particles or sorbed on particulate matter and may experience a resistance to volatilization attributable to the dissolution–partitioning process. Experimental observations in the laboratory and in the ocean are then compared with those expected theoretically.

Theoretical

A substance's diffusion rate through a medium is usually calculated by Fick's First Law in which

$$N = -DA\Delta C/\Delta y$$

where N is the flux (moles per second), D is a diffusivity (square metres per second), A is area (square metres), ΔC is the concentration difference (moles per cubic metre), and Δy is the diffusion path length (metres). If neither D nor Δy

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

[2]Author to whom correspondence should be addressed.

Printed in Canada (J6870)
Imprimé au Canada (J6870)

is known accurately they may be combined to give a mass transfer coefficient K (equal to $D/\Delta y$) with units of metres per second. K is thus the "piston velocity" with which the substance diffuses.

If diffusion takes place through a series of media (e.g. water and air) it is usual to assume that there is equilibrium at the interface; thus, the concentration profile is discontinuous. The substance may then move from low to high concentration at the interface. It is possible to write Fick's Law expressions for each phase or film and connect the interfacial concentration by a partition coefficient, as was done first by Whitman who introduced the "two-resistance theory" for gas–liquid exchange. Here, since there may be several series resistances, it is more convenient to introduce a general flux expression based on the concept of fugacity, as detailed in texts on thermodynamics (e.g. Prausnitz 1969) and discussed by Mackay (1979) and Mackay and Paterson (1981).

Fugacity (f) is an analog to chemical potential but is more convenient because it has units of pressure (pascals) and can thus be regarded as an "escaping tendency." It is usually linearly related to concentration (C) as

$$C = Zf$$

where Z is a fugacity capacity with units of moles per cubic metre per pascal. Values of Z can be estimated for each medium from physical chemical properties.

The advantage of using fugacity instead of concentration is that it is continuous over the diffusion path, i.e. a common value applies at the interface. Rewriting Fick's Law gives

$$N = -(DAZ/\Delta y)\Delta f$$

or

$$-(KAZ)\Delta f,$$

the groups in parentheses being effective conductivities.

It is more convenient to use resistances, since when diffusion processes occur in series the resistance terms become additive. We thus define a resistance r as

$$r = \Delta y/DZ$$

or

$$1/KZ,$$

hence

$$N = \Delta fA/r.$$

The resistance in a medium depends (as is obvious) on Δy, D, or K but also (and less obviously) on Z. The reason is that in phases of low Z, only a low concentration need develop to exert a high fugacity; thus, only low concentration gradients occur, and thus, diffusion rates are constrained. The general observation results that greatest diffusive resistance tends to lie in the phase in which concentration is lowest, or the substance is "least soluble," or Z is lowest.

For the air–water system, it is easily shown that in air, Z_A is $1/RT$ where R is the gas constant (8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$) and T is absolute temperature (Kelvin). Z_A is thus typically 4×10^{-4} $mol \cdot m^{-3} \cdot Pa^{-1}$. In water, Z_W is $1/H$ where H is the Henry's Law constant ($Pa \cdot m^3 \cdot mol^{-1}$) and is usually defined as the ratio of the substance's vapor pressure P^S (pascals) to aqueous solubility C^S (moles per cubic metre); i.e. H is P^S/C^S. Invoking air and water mass transfer coefficients K_A and K_W gives

$$\text{Air resistance } r_A = 1/K_A Z_A = RT/K_A$$

$$\text{Water resistance } r_W = 1/K_W Z_W = H/K_W$$

$$\text{Total resistance} = RT/K_A + H/K_W.$$

The flux is thus given by

$$N = -\Delta fA/(RT/K_A + H/K_W).$$

If the water concentration is C_W (thus, f_W is C_W/Z_W) and the air partial pressure is P_A (thus, f_A is P_A), then Δf is $C_W/Z_W - P_A$ or $C_W H - P_A$ and

$$N = -(C_W - P_A/H)k_{OW}A$$

where

$$1/k_{OW} = 1/K_W + RT/HK_A$$

and K_{OW} is an "overall" water phase mass transfer coefficient. This is the commonly used "two-resistance" equation first applied to oceanic conditions by Liss and Slater (1974) and later applied by Mackay and Leinonen (1975) to aquatic systems. It is a particular case of the more general case developed here.

In general, if there are several series resistances r_1, r_2, r_3, etc., with a common steady-state flux N then the individual fugacity driving forces Δf_1, Δf_2, etc., are given by

$$\Delta f_i = Nr_i/A_i.$$

But these Δf_i quantities must add to give the total or overall Δf_T; i.e.

$$\Delta f_T = \Delta f_1 + \Delta f_2 + \ldots$$

thus,

$$\Delta f_T = N(r_1/A_1 + r_2/A_2 \ldots) = N\sum_i (r_i/A_i)$$

or

$$N = \Delta f_T/\Sigma(r_i/A_i).$$

This is exactly analogous to the electrical series resistance system in which N is current, (r/A) is ohms, and Δf is voltage drop. Obviously, the most important resistance is the largest, which in this case tends to be the medium in which $D/\Delta y$, K, Z, or A is lowest.

The general approach is not necessary in the common two-resistance calculations, but other resistances may occur as

TABLE 1. Definition of resistances in terms of mass transfer coefficients (MTC), K, and fugacity capacities (FC), Z.

Resistance	Area	Definition	Explanation
Air surface resistance, r_A	A_H	$1/K_AZ_A$	K_A is air film MTC, Z_A is air FC
Water surface resistance, r_W	A_H	$1/K_WZ_W$	K_W is water film MTC, Z_W is water FC
Organic film, r_O	A_H	$\Delta y_O/D_OZ_F$	Δy is film thickness, D_O is diffusivity, Z_F is film FC
Water column resistance, r_C	A_H	$\Delta y_W/D_WZ_W$	Δy_W is water depth, D_W is vertical diffusivity
Oil drop internal resistance, r_I	A_P	$1/K_IZ_O$	K_I is internal drop MTC, Z_O is oil FC
Oil drop water film resistance, r_F	A_P	$1/K_FZ_W$	K_F is film resistance
Sorbed state resistance, r_S	A_P	$1/K_SZ_S$	K_S is sorbent release MTC, Z_S is sorbed state FC

follows and as shown in Table 1. (1) There may be a surface organic film of natural or anthropogenic origin which retards transfer. (2) In the case of oil, the hydrocarbon may be in particulate oil form in the water column as a result of natural or chemical dispersion; thus, it may experience a resistance inside the drop as it migrates to the drop surface and as it migrates through a stagnant film around the drop. (3) There may be a water column resistance associated with vertical diffusion to the surface. In stratified water there may be several such layers. (4) The substance may be sorbed on mineral or organic matter and may experience a resistance corresponding to the release from sorbed state. There may also be a film resistance in the water phase immediately surrounding the sorbent particle.

TRANSFER AREAS

The flux is normally calculated on a square metre basis, i.e. transfer is assumed to occur through a 1-m^2 horizontal area. This is acceptable for the air and water surface resistance, an organic film, and vertical diffusion in the water, but in the case of release from particles there may be a different exchange area (e.g. the total area of the particles). It follows that, for the first four resistances, the relevant area is A_H (the horizontal area in question) but for particles it is A_P, the particle area. If the volumetric concentration of particles is x $m^3 \cdot m^{-3}$ (x typically being $10^{-5}-10^{-6}$), of diameter d (metres), then each particle has an area of πd^2 and a volume of $\pi d^3/6$. There will thus be $6x/\pi d^3$ particles $\cdot m^{-3}$ with an area of $6x/d$ $m^2 \cdot m^{-3}$. If the total water volume in question is V m^3 then the total particle area, A_P, is $6xV/d$ m^2.

FLUX AND HALF-LIFE CALCULATION

Depending on the state of the substance the appropriate resistances can be selected from Table 1 and added to give the total resistance, $\Sigma(r_i/A_i)$. The flux, N, can then be calculated as $\Delta f_T/\Sigma(r_i/A_i)$ where Δf_T is the difference between the fugacity at source and destination (usually the atmosphere). The source fugacity is calculated from the source concentration, C, and the local source, Z, as C/Z, and the destination fugacity is calculated similarly, usually being the atmospheric partial pressure of the substance (often zero).

A differential equation can be set up and solved to give the residence time or half-life from a particular volume. This time is convenient in that it is easily grasped conceptually and gives an immediate indication of persistence and the role of volatilization relative to other degradation and dilution processes for which half-lives may also be available.

For convenience, we estimate half-lives separately for (*i*) volatilization from solution, (*ii*) transfer or dissolution from particles into water, and then (*iii*) for the combined processes of dissolution and volatilization.

VOLATILIZATION FROM SOLUTION

We consider a water volume V m^3 with a surface area A_H m^2. Considering, first, loss from solution to atmosphere at concentration C_W $mol \cdot m^{-3}$ the differential equation is

$$VdC_W/dt = N = -\Delta f A_H/r_T$$

where

$$\Delta f = C_W/Z_W - C_A/Z_A$$

and

$$r_T = 1/K_WZ_W + 1/K_AZ_A + \Delta y/D_VZ_W.$$

Here we ignore any surface organic film resistance. A constant area A_H applies to all resistances. The diffusion distance, Δy, is the mean depth of the volume in question and may be half of V/A_H if the volume in question extends to the surface. Rearranging gives

$$dC_W/(C_W - C_AZ_W/Z_A) = -A_H dt/[V(1/K_W + Z_W/K_AZ_A + \Delta y/D_V)] = -K_R dt$$

where K_R is the decay rate constant (per second); thus, the half-life, τ, is $0.69/K_R$ or

$$0.69V(1/K_W + Z_W/K_AZ_A + \Delta y/D_V)/A_H.$$

If the area extends to the surface, V/A_H is Y, the total depth, and because Z_W/Z_A is RT/H or RTC^S/P^S, τ_V becomes

$$(1) \quad \tau_V = 0.69Y(1/K_W + RTC^S/P^SK_A + \Delta y/D_V).$$

Interestingly, when H or P^S/C^S is large the group containing K_A becomes negligible and the rate ceases to be influenced by H; thus, the volatilization rate is independent of the substance's vapor pressure or solubility, the flux being limited by water phase diffusion. For example, substances such as heptane, benzene, and decane should exhibit similar half-lives when volatilizing from solution.

TABLE 2. Properties of the hydrocarbons.

Compound	Molecular weight ($g \cdot mol^{-1}$)	Seawater solubility ($g \cdot m^{-3}$)	Vapour pressure at 20°C (Pa)	Henry's Law constant ($kPa \cdot m^3 \cdot mol^{-1}$)	K_{OW}
Methylcyclohexane	98.19	10.5(25°C)[a]	4 562.8	42.7	5.5×10^4
n-Hexane	86.17	8.95(25°C)	1.6×10^4	1788	5.3×10^4
n-Octane	114.23	0.495(20°C)[a]	1 467	338	1.1×10^6
n-Decane	142.28	0.087(20°C)	360	589	1.4×10^7
Dodecane	170.33	0.0029(25°C)	9.78	574	2.0×10^8
Tetradecane	198.38	0.0017(25°C)	0.75	88	3.5×10^8
Benzene	78.11	1391(25°C)	10 132	0.569	494
Toluene	92.13	402(25°C)	2 933	0.67	1 683
p-Xylene	106.17	110.9(25°C)	866.6	0.83	4 350
1,3,5-Trimethylbenzene	120.19	31.3(25°C)	277.9	1.07	17 950
Naphthalene	128.19	22(25°C)	6.53	0.038	32 862
Phenanthrene	178.23	0.71(25°C)	0.0144	0.0036	8.3×10^5

[a]Estimated values; taken to be 75% of the aqueous solubilities at 25°C.

DISSOLUTION RATE FROM PARTICLES IN THE WATER COLUMN

If the volatilizing substance is present in solution in particles of dispersed oil in the water column there may be a volatilization delay corresponding to the dissolution process; thus, it is essential to calculate the corresponding half-life of this process. If this is long and the process slow, it will impede volatilization from solution. Conversely, if dissolution is rapid, the extra delay may be insignificant.

Considering a drop of oil of diameter d and volume V_O in water that contains a solute at concentration C_O in the oil, the dissolution rate will be given by

$$V_O\, dC_O/dt = N = -\Delta f A_P/(r_I + r_F)$$

where Δf is $(C_O/Z_O - C_W/Z_W)$. Assuming that C_W is constant and expressing V_O and A_P in terms of diameter d, it can be shown that the half-life for dissolution will be

$$\tau_D = 0.69d(1/K_I + Z_O/K_F Z_W)/6.$$

It is believed that K_I and K_F should have values of the order of 10^{-3}–10^{-4} $m \cdot s^{-1}$ based on the observation that the Sherwood number for diffusion from small drops is approximately 2; thus, for a 10-μm drop, K_F should be approximately twice the solute molecular diffusivity in water divided by the drop diameter. Since a typical diffusivity is 10^{-9} $m^2 \cdot s^{-1}$ and d is 10^{-5} m, K_F should be 2×10^{-4} $m \cdot s^{-1}$. K_I will probably be lower, a convenient estimate being simply the ratio of diffusivity in oil to drop diameter, i.e. typically 0.5×10^{-4} $m \cdot s^{-1}$ (Sherwood et al. 1975). Inserting such values shows that the internal oil drop resistance term must be negligible because the group Z_O/Z_W typically has a value of 10^3–10^6; thus, $1/K_I \ll Z_O/K_F Z_W$. The implication is that the resistance experienced in the water film around the particle greatly exceeds that in the particle.

If a Sherwood number of 2.0 is assumed, K_F can be expressed as $2D_M/d$ where D_M is the molecular diffusivity. Z_O/Z_W is K_{OW}, the oil–water partition coefficient, which is also $1/\nu C^S$ where ν is the solute molar volume (cubic metres per mole). Further substitution shows that $1/\nu C^S$ is simply ρ/S where ρ is the solute density (grams per cubic metre) and S is the aqueous solubility (grams per cubic metre). K_{OW} (Table 2) is usually very large, especially for alkanes.

The dissolution half-life expression thus simplifies to

$$\tau_D = 0.69d^2 K_{OW}/(12D_M). \quad (2)$$

A typical diffusivity is 10^{-9} $m^2 \cdot s^{-1}$; thus, if K_{OW} is 10^5 and d is 10^{-5}, the half-life is 10 min. The half-life is very sensitive to diameter and may be quite long for alkanes of high K_{OW} value.

VOLATILIZATION FROM MIXTURES OF PARTICLES AND SOLUTION

This situation is quite complex, the corresponding differential equations being the simultaneous pair

$$V_O dC_O/dt = -(C_O/Z_O - C_W/Z_W)A_P/(r_I + r_F)$$

$$V_W dC_W/dt = -(C_W/Z_W - C_A/Z_A)A_H/(r_W + r_A + r_S) - V_O dC_O/dt.$$

Here, V_O is the oil particle volume present in V_W m^3 of water.

Rigorous solution of this pair leads to rather complex expressions. A simpler approach is to examine two limiting solutions and argue that intermediate solutions can be deduced from these limits.

The first limit occurs when dissolution from drops is rapid compared with volatilization and it can be assumed that C_O and C_W will be in instantaneous equilibrium; i.e. C_O/C_W is Z_O/Z_W; thus, $C_W Z_O/Z_W$ can be substituted for C_O in the second equation yielding

$$(V_W + V_O Z_O/Z_W)dC_W/dt = -(C_W/Z_W - C_A/Z_A)A_H/(r_W + r_A + r_S)$$

and the corresponding half-life is

$$\tau_P = 0.69(r_W + r_A + r_S)(V_W Z_W + V_O Z_O)/A_H \quad (3)$$

which reduces to equation 1 when V_O is zero.

The implication is that τ_P is lengthened by the factor $(V_W Z_W + V_O Z_O)/(V_W Z_W)$ or $(1 + V_O Z_O/V_W Z_W)$ or $(1 + xK_{OW})$ which corresponds to the ratio of the total amount of solute present to that in solution. The ratio V_O/V_W is the volume fraction of oil in water, x, while Z_O/Z_W is the solute's oil–water partial coefficient, K_{OW}, which can be readily estimated as $1/vC^S$ or ρ/S.

Measurements of volatilization rate in the presence of oil particles should thus yield longer half-lives, especially for less soluble compounds, because much of the compound may be in the oil phase and thus does not exert a fugacity in solution. Experimentally, it is not easy to measure C_O or C_W individually, the total hydrocarbon concentration usually being measured.

The second limit occurs when dissolution from drops is slow compared with volatilization and C_W approaches zero. The time for dissolution, τ_D, will then be longer than τ_V for volatilization and equation 2 approximates the total half-life.

It is thus suggested that half-lives be evaluated separately using equations 1, 2, and 3 and the total half-life estimated as the sum of τ_D (equation 2) and τ_P (equation 3). The controlling process can be identified as that corresponding to the longest time. A similar expression can be developed for volatilization from sorbed form in which case a sorption partition coefficient K_P replaces K_{OW}.

Experimental

Having developed this theoretical framework to describe the volatilization half-life from solution and dispersion it is interesting to test the predictions against experimental observations. Some experiments were thus undertaken in a small laboratory apparatus to determine the half-life, τ. Comparison is also possible with data for oceanic conditions obtained by McAuliffe et al. (1980) in which concentrations were measured under dispersed experimental oil spills.

Apparatus

A modified version of a dispersant effectiveness apparatus described by Mackay and Szeto (1981) was used. Six litres of seawater was contained in a 30-cm-diameter glass tank placed in a constant temperature bath at 20°C. Air was blown tangentially over the water surface to create a swirling motion. The air flow was measured by an orifice meter with a pressure drop of 3.5 cmH_2O.

Materials

The hydrocarbons used were methylcyclohexane (Phillips, pure grade), *n*-hexane (Fisher, 99 mol%), *n*-octane (Eastman, practical), *n*-decane (Eastman), dodecane (Eastman), benzene (Fisher, 99 mol%), toluene (Fisher, 99 mol%), *p*-xylene (BDH), 1,3,5-trimethylbenzene (Aldrich, >99%), naphthalene (Fisher, certified), and tetradecane (Eastman, >97%). These (5% v/v, except tetradecane) were mixed to give a "synthetic" crude oil. Phenanthrene (Eastman) was also used but was added directly to the water.

Procedure

Solution tests — Saturated solution was prepared by adding an excess quantity of hydrocarbon to 30 g $NaCl \cdot L^{-1}$ and stirred with a Teflon-coated magnetic bar for 24 h. This was then diluted to 6 L and poured into a tank. Sampling was started only after the wave pattern in the tank had stabilized. Samples were periodically taken by syringe at middepth for 120 min and were analyzed by gas chromatography, or by fluorescence in the case of phenanthrene.

Dispersion — A mixture of hydrocarbons was premixed with the Exxon oil spill dispersant Corexit 9527 in a volume ratio of 50:1, respectively. One millilitre of this mixture was injected into 2 L of artificial seawater using a syringe to form a dispersion of small oil drops in water. The dispersed solution was diluted to 6 L. The sampling procedure was the same as for the true solution except that there was an oil particle phase in the sample. The experimental time was 420 min. The samples were analyzed by gas chromatography.

Analysis

A Hewlett-Packard 7675A purge and trap sampler and 5840 A gas chromatograph were used for analysis. The operating conditions were as follows: purge time 20 min; desorb temperature 200°C; carrier gas N_2 at 5 $mL \cdot min^{-1}$; detector FID at 300°C; column WCOT SE-30 (Alltech Associates Inc.), 0.5-mm inside diameter, 50 m long. Temperature programing was from 40°C at 5° $\cdot min^{-1}$ after a 10-min delay with 20 min at 200°C.

The response factor of each hydrocarbon with respect to benzene was determined by serial dilution of the mixture in methanol. Calibration was by serial dilution of a saturated benzene solution.

An Aminco-Bowman spectrophotofluorometer (American Instruments Ltd.) was used to analyze samples containing phenanthrene. An emission spectrum was obtained at an excitation wavelength of 255 nm. Calibration was by serial dilution of saturated phenanthrene solutions.

Results and Discussion

Laboratory Volatilization from Solution

All hydrocarbons, except phenanthrene, exhibited a similar slope of log C plotted against time, corresponding to a mean half-life of 24.3 min (Fig. 1). The concentrations of the alkanes were too low to measure accurately.

The exceptional hydrocarbon phenanthrene has a low Henry's Constant; thus, it experiences an air phase resistance in addition to the water phase resistance. In this case, the water depth, Y, is 8.6 cm; thus, Δy can be taken as 4.3 cm. D_V is very large, possibly 10 $cm^2 \cdot s^{-1}$, because of the substantial mixing.

The data are consistent with equation 1 developed earlier if these values are adopted and values are assigned to K_W of 4×10^{-5} $m \cdot s^{-1}$ (14.4 $cm \cdot h^{-1}$) and K_A of 8×10^{-3} $m \cdot s^{-1}$ (2880 $cm \cdot h^{-1}$). Both values are similar to those quoted for oceanic conditions (Liss and Slater 1974); thus, the laboratory

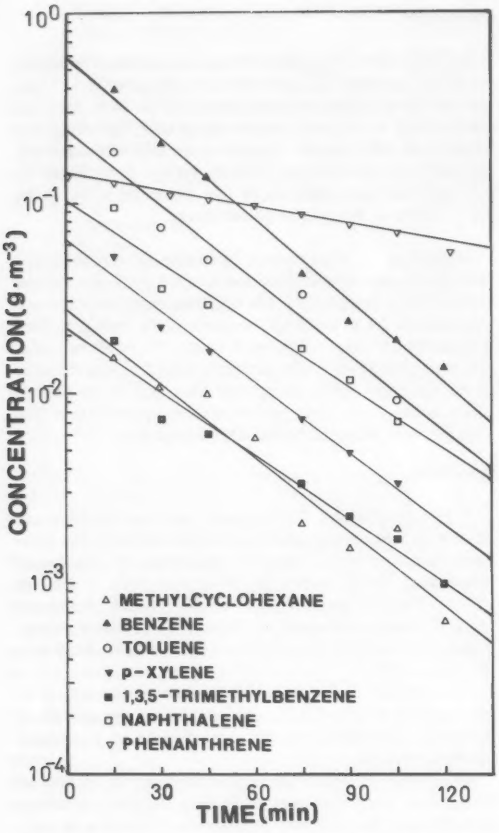

FIG. 1. Plot of log concentration of various hydrocarbons vs time for volatilization from solution.

system apparently can simulate natural volatilization rates.

Equation 1 can thus be used to correlate the experimental data. Table 3 gives the calculated half-lives using these K_A and K_W values. The agreement is very satisfactory. In all cases the water column resistance term, $\Delta y/D_V$, is negligible. Only in the case of phenanthrene, and to a lesser extent naphthalene, is the air phase resistance important.

It is concluded that the laboratory system can be used to investigate the volatilization behaviour of contaminants from ocean surface waters. It may be particularly useful for investigating the volatilization characteristics of new chemicals such as pesticides for which no reliable data are available and for explaining the effects of variable salinity and temperature.

Recent studies of the volatilization process (Mackay et al. 1982) have resulted in correlations for K_W and K_A as a function of wind speed, temperature, and solute properties, notably diffusivity; thus, it is possible to calculate resistances and half-lives for a wide variety of oceanic environmental conditions.

Laboratory Volatilization from Particles

In this case (Fig. 2), data could be obtained for the alkanes because of the higher concentrations. Dispersion half-lives are more variable and longer than solution half-lives. The data show a definite trend for high solubility (e.g. benzene and toluene) to cause short half-lives. The alkane half-lives increase with increasing carbon number, which corresponds to lower solubility.

A detailed interpretation of these data would require accurate values for the particle diameters, since the dissolution time is very sensitive to diameter. From particle size measurements in similar systems using a Coulter counter, it is believed that the mean diameter is of the order of 1 μm. Negligible dissolution delays would be encountered for the aromatics since τ_D calculated from equation 2 is typically less than 1 min. The alkanes should show some delay; e.g. a 9-min delay may occur with decane.

The increase in half-life due to the term $1 + xK_{OW}$, i.e. the "storage" of hydrocarbon in the oil phase, can be estimated approximately using a mean x value of 10^{-6}, which applied

TABLE 3. Calculated and experimental volatilization half-lives.

Compound	Experimental solution half-life (min)	Calculated solution half-life (min)	Experimental dispersion half-life (min)
Methylcyclohexane	23	24	38
n-Octane	—	24	63
n-Decane	—	24	97
Dodecane	—	24	100
Tetradecane	—	24	131
Benzene	21	25	39
Toluene	23	25	41
p-Xylene	24	25	44
1,3,5-Trimethylbenzene	27	25	46
Naphthalene	28	32	59
Phenanthrene	97	108	—

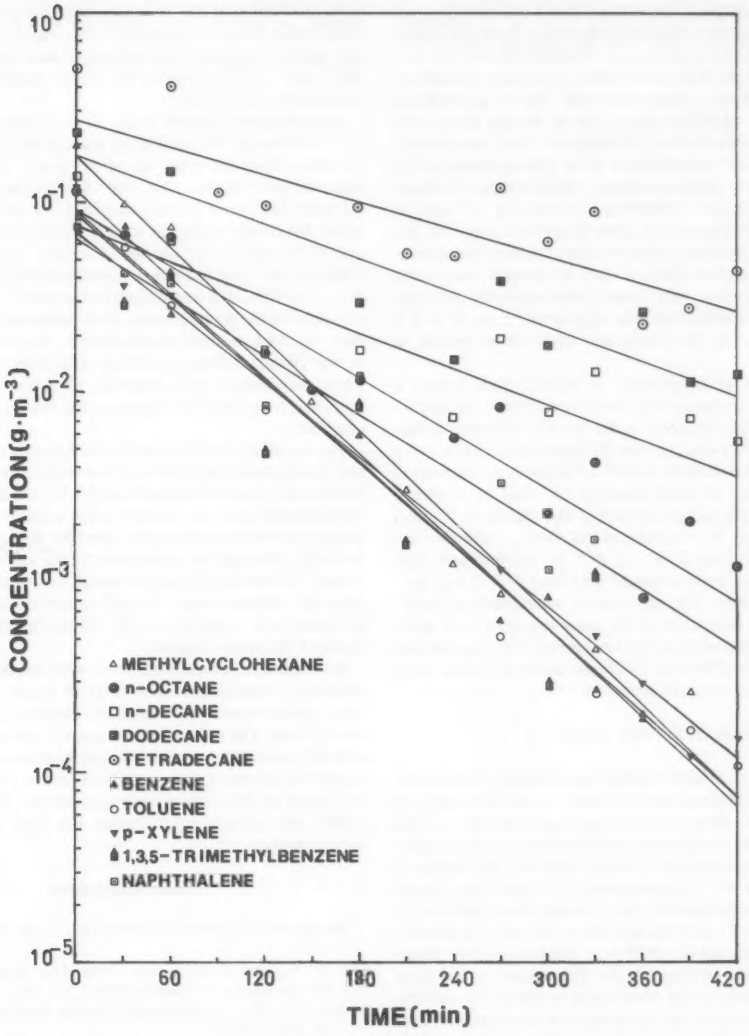

FIG. 2. Plot of log concentration of various hydrocarbons vs time for volatilization from dispersion.

during the experiment. The interesting conclusion is that only when K_{ow} exceeds 10^6 does an appreciable fraction of the hydrocarbon reside in the oil phase. Essentially all the aromatics must be in solution, not in the dispersion. Only the alkanes above octane should show an appreciable delay due to this factor. For example, $1 + xK_{ow}$ for octane will be approximately 2.4; thus, a half-life approximately double that of benzene is expected. The experimental ratio was 1.6 which is in fair agreement. Agreement is less satisfactory for the higher alkanes which have shorter half-lives than is predicted.

We believe that the increase in half-life of the aromatics from approximately 24 to 42 min is due to the presence of surfactant and possibly oil at the air–water interface, which both damp turbulence and thus reduce the water-side transfer coefficient. This was confirmed experimentally by adding a small quantity of surfactant to the system during benzene volatilization, resulting in an approximate halving of K_w and a doubling of τ_V.

The general conclusions are that for aromatics and other solutes of solubility greater than $1\ g \cdot m^{-3}$, there is no

appreciable delay due to dissolution from 1-μm particles, nor is there an appreciable fraction of the solute in the oil phase, at least when the oil phase is at a concentration of 1 $g \cdot m^{-3}$. Volatilization from such systems should proceed as rapidly as occurs from solution, except that there may be a turbulence damping effect. Half-lives in the 10- to 50-min range seem likely. Compounds such as phenanthrene with low Henry's Law constants will experience a delay corresponding to the presence of an air phase resistance. Volatilization of alkanes and other solutes with solubilities less than 1 $g \cdot m^{-3}$ will be delayed by a combination of slow dissolution from the dispersion and the tendency for these solutes to partition into the oil phase. Dissolution times of tens of minutes may occur from 1-μm particles, with longer times applying to larger particles. The experimental data suggest half-lives of 1−2 h in the range octane to tetradecane when oil is present at 1 $g \cdot m^{-3}$.

The presence of a spectrum of particle sizes causes a complication. Dissolution will be very rapid from the smaller particles and will "accelerate" as the particles become smaller; thus, there will be a tendency for the larger particles to survive longer. One effect could be a rapid initial decay by dissolution and volatilization of small particles followed by a slower decay of the larger residual particles. The data in Fig. 2 suggest that this may be occurring in that the C_{14} concentration dropped rapidly from 5 to 1 $g \cdot m^{-3}$ in 100 min and then tended to remain more constant (reaching 0.2−0.4 $g \cdot m^{-3}$ some 300 min later). The early period corresponds to a half-life of some 40 min which is the value expected from solution volatilization, whereas the later period corresponds to a half-life of nearly 200 min. Dodecane shows a similar trend although the data are quite scattered.

Oceanic Volatilization from Particles

McAuliffe et al. (1980) reported concentration data for low molecular weight hydrocarbons in water samples at a depth of 1 m at times from 18 to 110 min following dispersion. In that case an additional complication was the reduction in concentration due to horizontal and vertical diffusion. The aromatics exhibited a half-life of approximately 18 min which could be interpreted approximately as a volatilization half-life of 36 min coupled to a dilution half-life of 36 min. The alkanes exhibited a longer half-life of 29 min which is possibly attributable to delayed volatilization due to partitioning and slow dissolution. An interesting observation in that study was that the relative amounts of the compounds in the water differed greatly from those found in water saturated with the oil. The more soluble hydrocarbons tended to be present in the water at lower relative concentrations. McAuliffe et al. (1980) interpreted this as implying that the measured concentrations were essentially of particulate oil which had been preferentially depleted of the more soluble compounds.

Our work suggests that at the relatively low total oil concentrations encountered, most of the low molecular weight hydrocarbons may have been in solution and were volatilizing at essentially equal half-lives of some tens of minutes. The reason for the difference in relative amounts was that immediately following dispersion there was very rapid dissolution and volatilization of the more soluble compounds at the surface with a half-life of only a few minutes. The less soluble hydrocarbons experienced less rapid dissolution and less partitioning into water because of their high K_{ow} values; thus, they were conveyed to greater depths from which volatilization is slower.

An impressive fraction of the oil must have evaporated, as is illustrated by the following calculation. Toluene had a solubility from the crude oil of 5.6 $g \cdot m^{-3}$ or 1.4% of the value for pure toluene; thus, the toluene concentration in the oil must have been of the order of 1.4% on a molar basis. After dispersion when the total oil concentration was 11.0 and 17.8 $g \cdot m^{-3}$, the amount of toluene was 0.00375 and 0.0035 $g \cdot m^{-3}$; i.e. the ratio of toluene to total oil was approximately 0.03%. The implication is that only 2% of the toluene remained in the water column, 98% having evaporated either from the slick or from the dispersion. It is conceivable that in the 20 min following spillage and dispersion there was rapid evaporation with a half-life of a few minutes corresponding for example to volatilization from a depth of a few centimetres.

The conclusion is that volatilization plays a very significant role in mitigating the effects of low molecular weight hydrocarbons on water column biota even when the oil is dispersed. The transient processes occurring immediately following dispersion are very complex and cannot yet be described mathematically although the qualitative trends are consistent with theory. The later and slower evaporative loss of dissolved and dispersed hydrocarbons is well described by the theory presented here, a half-life of 20−60 min applying to the top metre of the water column.

In conclusion, a theoretical framework has been derived for calculating volatilization half-lives of organic contaminants from surface waters for solutes in dissolved, particulate, or sorbed form. The exploratory laboratory data and the oceanic data are consistent with the theoretical postulations, lending support to the use of these equations for the prediction of the magnitude of the various resistance terms, which, in total, control the solute's volatilization rate and its half-life in surface waters.

Acknowledgment

The authors are grateful to Imperial Oil Ltd. for financial support.

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Distributions and Fate of Volatile Organic Compounds in Narragansett Bay, Rhode Island[1]

S. G. WAKEHAM, J. T. GOODWIN, AND A. C. DAVIS

Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

WAKEHAM, S. G., J. T. GOODWIN, AND A. C. DAVIS. 1983. Distributions and fate of volatile organic compounds in Narragansett Bay, Rhode Island. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 304–321.

A wide range of volatile organic compounds (VOC) were measured in the water column along a north–south transect in Narragansett Bay, Rhode Island, during two summers and two winters. The dominant VOC are chlorinated C_2-hydrocarbons, chlorobenzenes, and aromatic hydrocarbons. Major sources for these anthropogenic compounds are municipal and industrial wastewaters discharged into the upper bay. Concentration trends along the transect are variable depending on the compound class and the season of sampling, indicating that different processes control the distributions of different compounds. Volatilization apparently is a major removal process for all VOC. Calculations suggest water column residence times with respect to volatilization of 150–300 h in Narragansett Bay. Biodegradation, particularly in summer, is important for aromatic hydrocarbons, which are degraded in a few days. Sorption onto particulate matter and eventual sedimentation is minor, except for the higher molecular weight alkanes.

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Une gamme étendue de composés organiques volatils (COV) ont été mesurés dans la colonne d'eau le long d'une section nord–sud dans la baie de Narragansett, au Rhode Island, pendant deux étés et deux hivers. Les COV dominants sont les hydrocarbures-C_2 chlorés, les chlorobenzènes et les hydrocarbures aromatiques. Les eaux usées municipales et industrielles déversées dans le haut de la baie sont les principales sources de substances dérivées d'activités humaines. Les concentrations le long de la section ont des tendances variables selon la classe du composé et la saison d'échantillonnage, signe que des processus différents règlent la répartition des divers composés. La volitilisation semble être un agent majeur d'enlèvement de tous les COV. Certains calculs laissent supposer que le temps de résidence dans la colonne d'eau en ce qui concerne la volatilisation est de 150 à 300 h dans la baie de Narragansett. La biodégradation, particulièrement en été, joue un rôle important pour les hydrocarbures aromatiques, qui se dégradent en quelques jours. La sorption sur la matière particulaire et une sédimentation éventuelle ont peu d'importance, sauf pour les alcanes de haut poids moléculaire.

Received March 24, 1982
Accepted October 4, 1982

Reçu le 24 mars 1982
Accepté le 4 octobre 1982

COASTAL waters receive a variety of organic pollutants from municipal and industrial sources. A subset of these chemicals, volatile organic compounds (VOC or "volatiles") have molecular structures of low to medium polarity in the volatility range bracketed by *n*-hexane and *n*-octadecane. Since many of these compounds are toxic and thus potentially harmful to marine ecosystems and possibly humans as well (Malins 1977; Wolfe 1977; Jolley 1978; Jolley et al. 1978; NAS 1978), there is substantial interest in elucidating the sources, persistance, transport mechanisms, and fate of these chemicals in coastal areas.

Several approaches have been used to study VOC in the coastal environment. Gschwend and co-workers (Gschwend 1979, Schwarzenbach et al. 1978; Gschwend et al. 1982; Mantoura et al. 1982) evaluated sources and sinks of alkanes, alkylaromatic hydrocarbons, aldehydes, and alkylsulfides

[1]Woods Hole Oceanographic Institution Contribution No. 5111. This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6885)
Imprimé au Canada (J6885)

over a 2-yr period at a single site in Vineyard Sound, MA. Alternatively, Sauer and co-workers (Sauer et al. 1978, Sauer 1978, 1980, 1981) measured aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, and aldehydes at a number of coastal, shelf, and open ocean sites in the Gulf of Mexico, but on a more limited time scale. Helz and Hsu (1978) determined C_1- and C_2-halocarbons in Chesapeake Bay along a salinity and pollution gradient from a point source. Field measurements are necessary to verify the fate of VOC predicted by laboratory studies and model calculations (Dilling et al. 1975; Dilling et al. 1976; Dilling 1977; Bouwer et al. 1981; Mackay and Wolkoff 1973; Mackay and Leinonen 1975; Mackay 1978; Smith et al. 1980; Matter-Müller et al. 1981).

We have been addressing the sources, fates, and transport of VOC in the coastal environment in two ways. To assess spatial and temporal variations in distributions of VOC in an estuary, we made a series of field measurements on a transect along a salinity–pollution gradient in Narragansett Bay, Rhode Island. As field studies alone cannot lead to a complete understanding of the biogeochemistry of VOC, we have also been conducting controlled microcosm VOC experiments at the Marine Ecosystems Research Laboratory (MERL), University of Rhode Island (Pilson et al. 1977; Santschi 1982). These experiments help to better define the fate and persistence of volatiles in the estuary and to verify conclusions drawn from field observations. In this paper we report distributions, sources, and probable fates of VOC in Narragansett Bay based on field studies. Initial results of the microcosm experiments have been reported by Wakeham et al. (1982a), and further details will be the subject of a future paper.

Experimental

Narragansett Bay is a temperate, well-mixed, plankton-based estuarine ecosystem on the Rhode Island coast (Fig. 1). Its physical and biological characteristics are described by Hicks (1959) and Kremner and Nixon (1978). Narragansett Bay has a length of about 45 km, a maximum width of 18 km, an area of 270 km^2, and a volume of approximately 2.6×10^9 m^3. Mean depth in the bay is 9 m and averages 7.5 and 15.2 m in West and East Passages, respectively. Tides are semidiurnal with mean ranges of 1.1 m at the mouth of the bay and 1.4 m at the head of the bay. The tidal prism is about 13% of the mean volume of Narragansett Bay and greater than 250 times the mean total river inflow over a tidal cycle. Residence time for water in the bay is estimated at about 30 d, and outflow into Rhode Island Sound is split approximately 40% through West Passage and 60% through East Passage. The bay is well mixed by a combination of winds and tides so that only in summer is there a significant thermocline and salinity gradient, and then only in the upper bay (Wakeham et al. 1982b). Annual water temperatures range from about −0.5 to 24°C, and salinities vary from about 20‰ in the Providence River to 32–33‰ at the mouth of the bay.

The dominant freshwater input to Narragansett Bay is the Providence River with a mean annual flow of 1×10^9 m^3, approximately 10% of the total freshwater input to the Bay. Three sewage treatment facilities discharge combined municipal, industrial, and stormwater effluents into the Providence River and upper Narragansett Bay. The largest is at Fields Point and delivers 2.3×10^5 m^3/yr, or 60% of the total sewage effluent entering the bay. Analysis of this effluent indicated that 100–500 t of petroleum hydrocarbons enters the Providence River annually (Farrington and Quinn 1973; Van Vleet and Quinn 1977); however, there are no reports in the literature of annual inputs of other organic compounds via the Fields Point effluent. Effluents from a small chemical manufacturing plant also enter Narragansett Bay between Sabin Point and Conimicut Point via the Pawtuxet River.

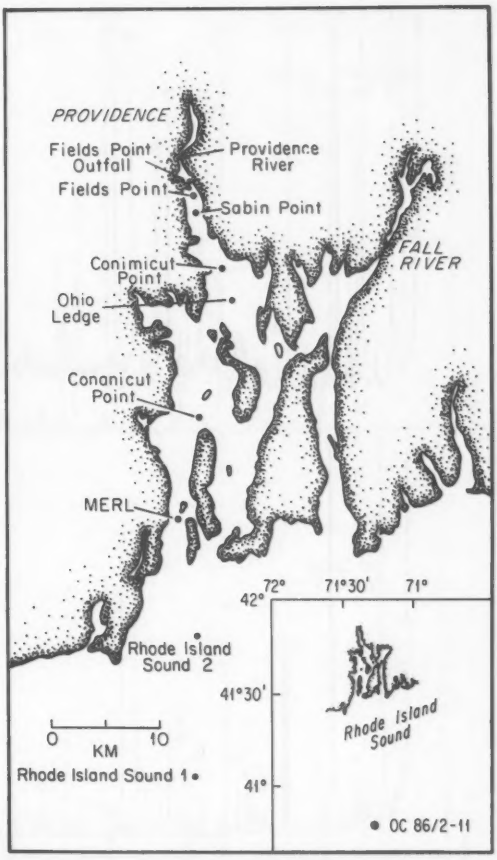

FIG. 1. Narragansett Bay, Rhode Island, and sampling locations for VOC.

SAMPLING

Water samples for analysis of VOC were collected along a north-to-south transect in Narragansett Bay (Fig. 1) during two summers (August 1, 1979, and July 22, 1980) and two

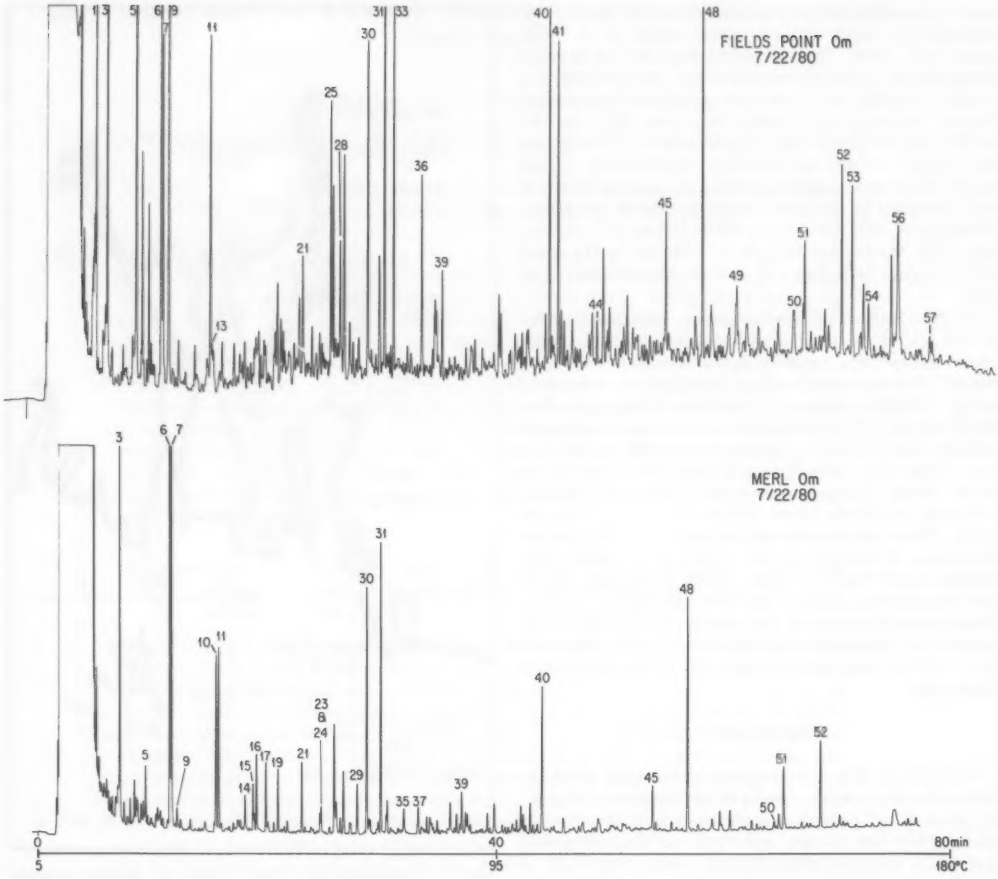

FIG. 2. Glass capillary gas chromatograms of FID signal of VOC in samples from Fields Point and MERL on July 22, 1980, and February 23, 1981. Chloroalkane standards in the Fields Point samples at 80 ng/L and in MERL samples at 10 ng/L. Gas chromatographic conditions given in text.

winters (February 25, 1980, and February 23, 1981). Stations were occupied at low tide ± 1 h. Samples were also obtained at two locations in Rhode Island Sound on July 21, 1980, and at a station about 70 km offshore (OC 86/2-11) on September 14, 1980. Near-surface and near-bottom samples were collected at all stations. The "Fields Point Outfall" samples discussed in the text do not represent actual effluents but rather samples collected in the outfall plume.

All Narragansett Bay samples and the surface samples from Rhode Island Sound were collected by lowering a clean, stoppered, air-filled 2- or 5-L glass bottle on a hand line to the prescribed depth, at which the stopper was removed by pulling a cord attached to the stopper. Sampling bottles were carefully rinsed on the deck of the ship (a clean laboratory would have been preferable but was not available) with water from the depth being sampled before collection of the sample for analysis. The filled bottle was recovered and quickly stoppered without headspace. Near-bottom samples in Rhode Island Sound and both samples at the offshore station were collected with a glass Bodman sampler (Gagosian et al. 1979) and carefully transferred to clean, rinsed 5-L bottles. All samples were returned to the laboratory as soon as possible for analysis within 72 h; any storage was at 4°C. No preservatives were used in the samples, but experiments showed that production or loss of most VOC was minimal during storage. Care was taken during all sampling to minimize contamination from the sea-surface microlayer and from fuel and exhaust from the ship by sampling about 0.5 m below the water surface and on the windward side of the boat. At the time of sampling, temperature and salinity measurements

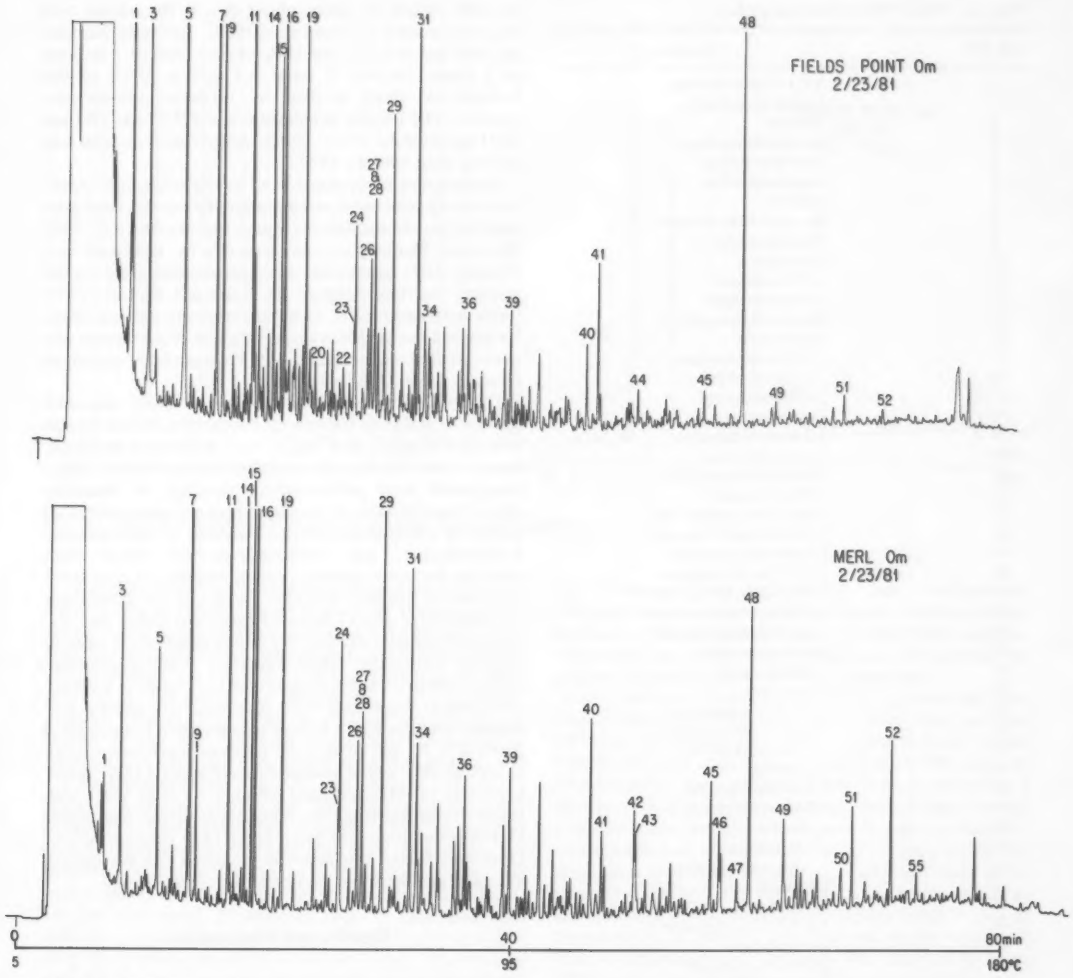

FIG. 2. (*Continued.*)

were made (Wakeham et al. 1982b).

ANALYSIS

Volatile organic compounds were isolated from unfiltered water samples and enriched by the closed-loop gas stripping – adsorption technique of Grob and Zürcher (1976). The volatile components were purged (stripped) in the sampling bottles by large volumes of headspace air, introduced in the laboratory, as finely divided bubbles, and adsorbed from the gas stream onto a trap containing 1.5 mg of activated charcoal. Stripping was for 2 h during which the sample was heated to 35°C to enhance volatilization and the gas stream leading to the charcoal trap was heated to 65°C to lower its relative humidity and thus optimize adsorption. The charcoal trap was subsequently extracted with about 15 μL of distilled carbon disulfide. An aliquot of the carbon disulfide extract was analyzed by high-resolution glass capillary gas chromatography using a Carlo Erba FTV 2150 gas chromatograph modified for simultaneous flame ionization (FID) and electron capture (ECD) (Carlo Erba ECD-HT 20 and 250 control module) detection. A glass capillary – platinum capillary effluent splitter, as described by Etzweiler and Neuner-Jehle (1973), was employed. Gas chromatographic separations of the VOC mixtures were made with a 40 m × 0.3 mm (inside diameter) capillary pretreated with barium carbonate and

TABLE 1. Major VOC in Narragansett Bay.

Peak No.	Compound
1	1,1,1-Trichloroethane
2	Carbon tetrachloride
3	Benzene
4	Bromochloromethane
5	Trichloroethylene
6	Dimethyldisulfide
7	Toluene
8	Bromotrichloromethane
9	Tetrachloroethylene
10	Octatriene[a]
11	1-Chlorohexane[b]
12	Dibromomethane
13	Bromodichloromethane
14	Ethylbenzene
15	1,4-Dimethylbenzene
16	1,3-Dimethylbenzene
17	2-Chlorothiophene
18	Chlorobenzene
19	1,2-Dimethylbenzene
20	Isopropylbenzene
21	Dibromochloromethane
22	*n*-Propylbenzene
23	1-Ethyl-4-methylbenzene
24	1-Ethyl-3-methylbenzene
25	Decahydronaphthalene
26	1,3,5-Trimethylbenzene
27	1-Ethyl-2-methylbenzene
28	1-Chloro-2-methylbenzene
29	1,2,4-Trimethylbenzene
30	Dimethyltrisulfide
31	1-Chlorooctane[b]
32	Bromoform
33	1,2,3-Trichloropropane
34	1,2,3-Trimethylbenzene
35	1,3-Dichlorobenzene
36	C_4-benzene
37	1,4-Dichlorobenzene
38	1,2-Dichlorobenzene
39	C_4-benzene
40	1-Chlorodecane[b]
41	1,2,4-Trichlorobenzene
42	Naphthalene
43	*n*-Tetradecane
44	1,2,3-Trichlorobenzene
45	*n*-Pentadecane
46	2-Methylnaphthalene
47	1-Methylnaphthalene
48	1-Chlorododecane[b]
49	*n*-Hexadecane
50	Pristane
51	*n*-Heptadecane
52	1-Chlorotetradecane[b]
53	1-Methyl-2-(4-methylphenoxy)benzene
54	Phytane
55	*n*-Octadecane
56	1-Methyl-3-(4-methylphenoxy)benzene
57	*n*-Nonadecane

[a]C_8H_{12} exact structure not known.
[b]Chloroalkane internal standards.

coated with Pluronics 121 (Grob and Grob 1977). Splitless injections were made with the column held at about 5°C in an ice bath. Following elution of the solvent, the column oven was programmed at 2°/min up to 180°C. Hydrogen was used as carrier gas at 0.5 kg/cm^2 back pressure (about 1.5 mL/min or a linear velocity of about 0.3 m/s at 35°C) so that *n*-octadecane eluted at about the maximum column temperature. The injector temperature was 225°C and FID and ECD temperatures were 250°C. Argon–methane make-up gas was used with the ECD.

Identification of the major VOC was by coinjection experiments using authentic standards and/or by computerized glass capillary gas chromatography – mass spectrometry (GC/MS). The same Pluronics column was directly interfaced to a Finnigan 3200 quadrupole mass spectrometer using a glass capillary interface designed by Blum and Richter (1977) (Frew and Sawdo 1980). Electron impact and methane chemical ionization mass spectra were obtained. Mass spectral data were acquired and processed with Finnigan 6000 and, more recently, Incos 2300 data systems.

The VOC were quantified using electronically measured (Columbia Scientific Instruments Supergrator 3) peak heights from the FID signal. Peak heights were preferred to peak areas because even with the high-resolution capillary column, many components were underresolved, resulting in inaccurate areas. Concentrations of sample components were calculated relative to chloroalkane internal standards (1-chlorohexane, 1-chlorodecane, and 1-chlorotetradecane) which were added to the water samples prior to stripping to correct for variations in stripping efficiency. A second set of standards (1-chlorooctane and 1-chlorododecane) was spiked onto the charcoal traps after stripping but before extraction to monitor stripping efficiency. Flame ionization detection response factors were determined using synthetic mixtures of a variety of volatiles. Recoveries were determined by spiking prestripped seawater with a suite of representative compounds at levels of 5, 10, and 50 ng/L per component and were usually better than 80% with reproducibilities of about ±15%. Detection limits by FID were about 0.5 ng/L for most VOC, with major exceptions being the halocarbons which had higher FID detection limits but much lower ECD detection limits. Laboratory blanks were routinely processed with the samples to ensure that there was no interfering contamination.

Results and Discussion

Distributions and Sources of VOC in Narragansett Bay

Volatile organic compounds recovered from Narragansett Bay water samples consisted of several hundred components (see typical FID chromatograms in Fig. 2). The major identified components (Table 1) include a variety of structural classes. Most of the minor components could not be conclusively identified. The ECD (Fig. 3) showed a number of halogenated compounds, primarily halomethanes, which were not evident in the FID traces. Specific ion searches of GC/MS data showed that most of the minor components eluting in the first half of the FID chromatograms were C_5- to C_{10}-cyclic and -acyclic hydrocarbons. Most components in the second half of these same chromatograms were alkylaromatic hydrocarbons (Fig. 4).

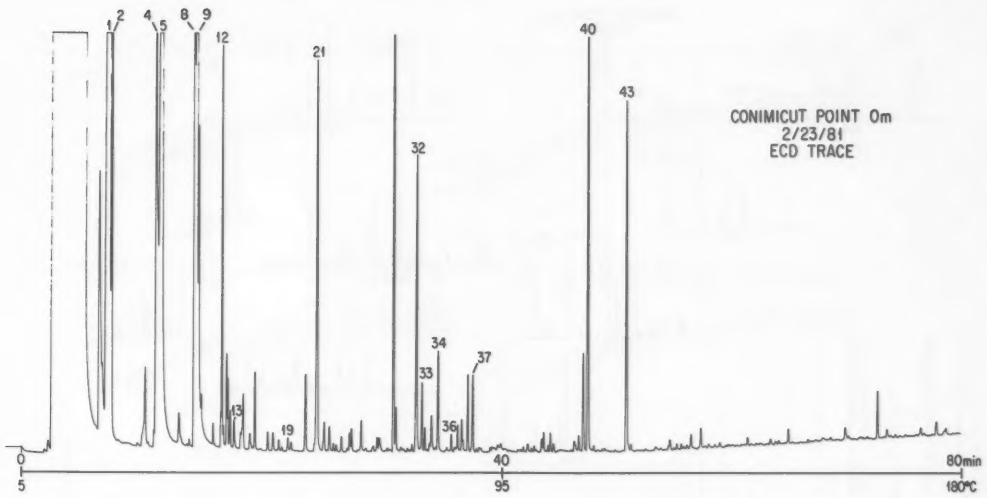

FIG. 3. ECD chromatogram of VOC in a Conimicut Point water sample.

Quantitative data were obtained for most of the volatiles in Table 1. The complete data set is given by Wakeham et al. (1982b). The most significant features are illustrated by profiles for six representative compounds from Narragansett Bay during summer and winter (Figs. 5–7). Tetrachloroethylene (Fig. 5) is characteristic of halogenated C_1- to C_3-hydrocarbons. Toluene (Fig. 5) was a dominant aromatic hydrocarbon in the bay, although many other alkylaromatic hydrocarbons were also present (Fig. 4). Chlorobenzene and 1,2,4-trichlorobenzene (Fig. 6) are typical chlorinated aromatic hydrocarbons, but they have different sources and behaviors in Narragansett Bay. Sources for VOC represented by tetrachloroethylene, the chlorobenzenes, and toluene are probably entirely anthropogenic in Narragansett Bay, and major inputs come from the Fields Point wastewater effluent. On the other hand, heptadecane (Fig. 7) may have both anthropogenic and biogenic sources, while dimethyldisulfide (Fig. 7) is predominantly biogenic in nature. Quantitative data for C_5- to C_{10}-cyclic and -acyclic hydrocarbons, and alkylaromatic hydrocarbons not listed in Table 1, were not determined. Aldehydes were present at levels of a few nanograms or less per litre in contrast with Vineyard Sound samples in which aldehydes were relatively abundant (Schwarzenbach et al. 1978, Gschwend et al. 1982).

HALOMETHANES

Chlorinated and brominated methanes were ubiquitous components of the VOC in Narragansett Bay but usually were detected only by ECD (Fig. 3). Bromoform (compound No. 32) was typical, with concentrations of about 2000 ng/L near the Fields Point Outfall, several hundred nanograms per litre in the upper bay (Fields Point, Sabin Point, and Conimicut Point), to tens of nanograms per litre in the lower bay (Conanicut Point and MERL). Other halomethanes (dibromomethane, bromotrichloromethane, dibromochloromethane, bromochloromethane, bromodichloromethane, chloroform, and carbon tetrachloride) were also present, but detailed distributions have not been determined.

Concentrations of halomethanes in Narragansett Bay were considerably lower than levels reported by Helz and Hsu (1978) in Chesapeake Bay where concentrations of carbon tetrachloride and chloroform ranged from 45 000 ng/L to "nondetectable" (no detection limits were given) along a salinity gradient (0–32‰) leading from a large sewage treatment plant. Brominated compounds were not reported. Concentrations of <1–20 ng/L for carbon tetrachloride and chloroform have been reported in coastal and open ocean seawater (Lovelock et al. 1973; Murray and Riley 1973; Su and Goldberg 1976). Eklund et al. (1982) found 5–200 ng bromoform/L in Swedish estuarine and coastal waters. A range of chloroform concentrations was observed by Sauer (1981) in the Gulf of Mexico, with low concentrations in the open ocean and higher concentrations in coastal waters influenced by anthropogenic sources.

Sources of halomethanes may be divided into three categories (NAS 1978): direct emissions during manufacture or industrial use, secondary production via water chlorination, and biogenic sources. Chlorinated methanes have industrial uses that readily lead to loss to the environment. In addition, chloroform is a major product of water chlorination by the haloform reaction (Jolley 1978; Jolley et al. 1978; NAS 1978; Helz and Hsu 1978). Brominated methanes, in contrast, have relatively minor industrial sources, and their formation during chlorination of freshwater is significantly less than for their chlorinated analogs. However, chlorination of seawater in which bromine (as hypobromous acid) is relatively abundant generates predominately bromoform (Helz and Hsu 1978;

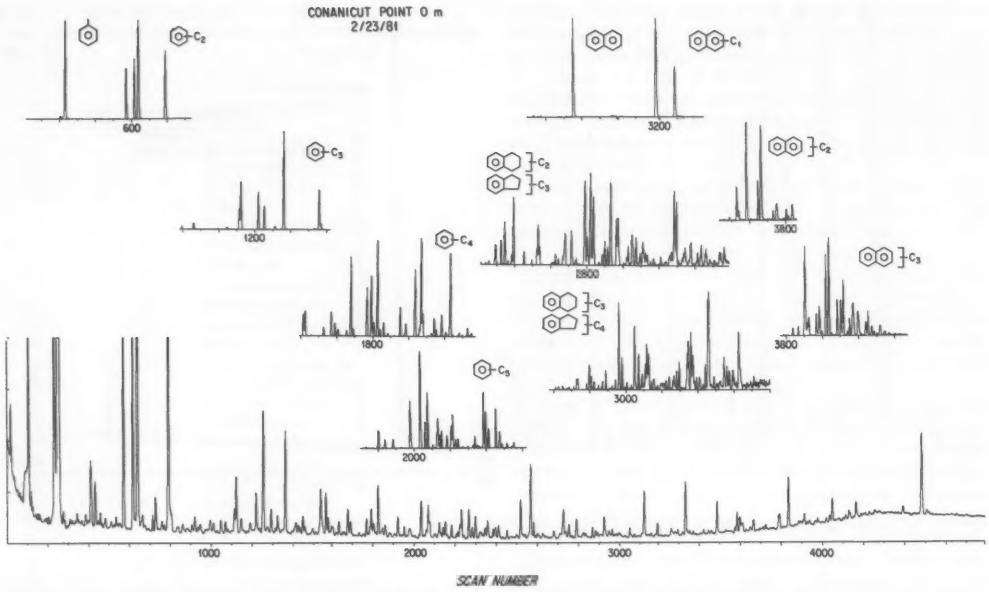

FIG. 4. Specific ion chromatograms of C_1- to C_5-alkylbenzenes, C_3- and C_4-alkylindenes, C_2- and C_3-alkyltetrahydronaphthalenes, and C_0- to C_3-alkylnaphthalenes in a Conanicut Point sample from February 23, 1981.

Bean et al. 1978). Bromoform concentrations of up to 60 000 ng/L were found in chlorinated seawater used as power plant coolant in Sweden (Eklund et al. 1982). Anthropogenic inputs of halocarbons, whether direct or secondary, probably account for most of the reported occurrences of these compounds in coastal seawater. Natural production of halocarbons, primarily bromoform and mixed bromochloro-compounds, have been described for several benthic algal species by Burreson et al. (1975, 1976), and Gschwend (1979). However, in Narragansett Bay, biogenic sources may play a minor role. Industrial discharges, chlorination of wastewaters at treatment plants, and secondary formation of halocarbons in the upper bay by chlorination–bromination reactions involving residual chlorine in discharged effluents are probably the dominant sources. Since the haloform reaction forms predominately haloforms (e.g. chloroform and bromoform), chlorination reactions may represent a major source of trihalomethanes, whereas dihalomethanes and tetrahalomethanes may have mostly industrial origins.

CHLORINATED C_2- AND C_3-HYDROCARBONS

1,1,1-Trichloroethane, trichloroethylene, and tetrachloroethylene were usually the most abundant VOC at the upper bay stations. Some samples also contained significant amounts of 1,2,3-trichloropropane (e.g. Fields Point, July 22, 1980, in Fig. 2). In the upper part of Narragansett Bay, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene (hereafter designated as chlorinated C_2-hydrocarbons) together accounted for 50–98% of the total VOC content (defined as the sum of all quantified components), whereas in the lower bay, they made up only 10–30% of the volatiles.

Concentration profiles for chlorinated C_2-hydrocarbons are represented by tetrachloroethylene in Fig. 5. Maximum concentrations were at the Fields Point Outfall, showing this to be a major source. Significantly lower concentrations in the Providence River upstream from Fields Point at low tide also show the outfall as the dominant source. This pattern is consistent with the widespread use of these compounds as industrial solvents and in chemical manufacturing processes. They are abundant in river and ground waters in industrialized areas (Zürcher and Giger 1976; Giger et al. 1978) and in industrial and municipal sewage effluents (Giger et al. 1978; Schwarzenbach et al. 1979; Young 1978). Chlorinated C_2 hydrocarbons are not significant products of water chlorination processes. Levels of the chlorinated C_2-hydrocarbons at the Sabin Point and Fields Point sites were unusually low on February 23, 1981 (Fig. 5). This is attributed to a heavy rainstorm the day before we sampled, resulting in a significant input of freshwater to the upper bay, as indicated by the salinities and temperatures for these two stations. Concentrations of the chlorinated C_2-hydrocarbons decreased significantly along the transect. Concentration gradients (comparing upper bay stations with lower bay stations) in summer were markedly greater than in winter. Absolute concentrations in the lower bay were generally higher in winter compared with summer, whereas levels in the upper bay were less variable

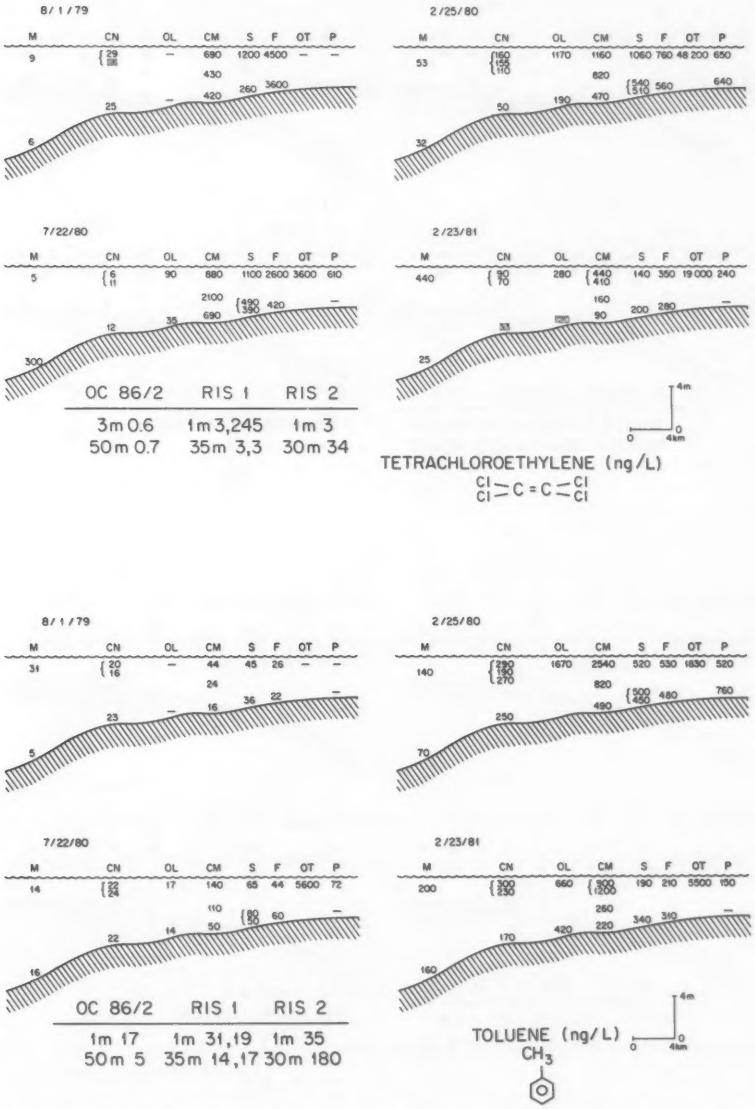

FIG. 5. Tetrachloroethylene and toluene concentrations (nanograms per litre) in Narragansett Bay. Station locations corresponding to Fig. 1 and Table 1 are as follows: OC 86/2-11 = Oceanus 86/2 station 11; RIS 1 = Rhode Island Sound 1; RIS 2 = Rhode Island Sound 2; M = MERL; CN = Conanicut Point; OL = Ohio Ledge; CM = Conimicut Point; S = Sabin Point; F = Fields Point; OT = Fields Point Outfall; P = Providence River.

seasonally.

The range of chlorinated C_2 hydrocarbon concentrations in upper Narragansett Bay are comparable with levels in Chesapeake Bay (up to 50 000 ng/L) (Helz and Hsu 1978) and in Liverpool Bay (up to 3600 ng/L) (Pearson and McConnell 1975), both of which are near municipal areas. The lower

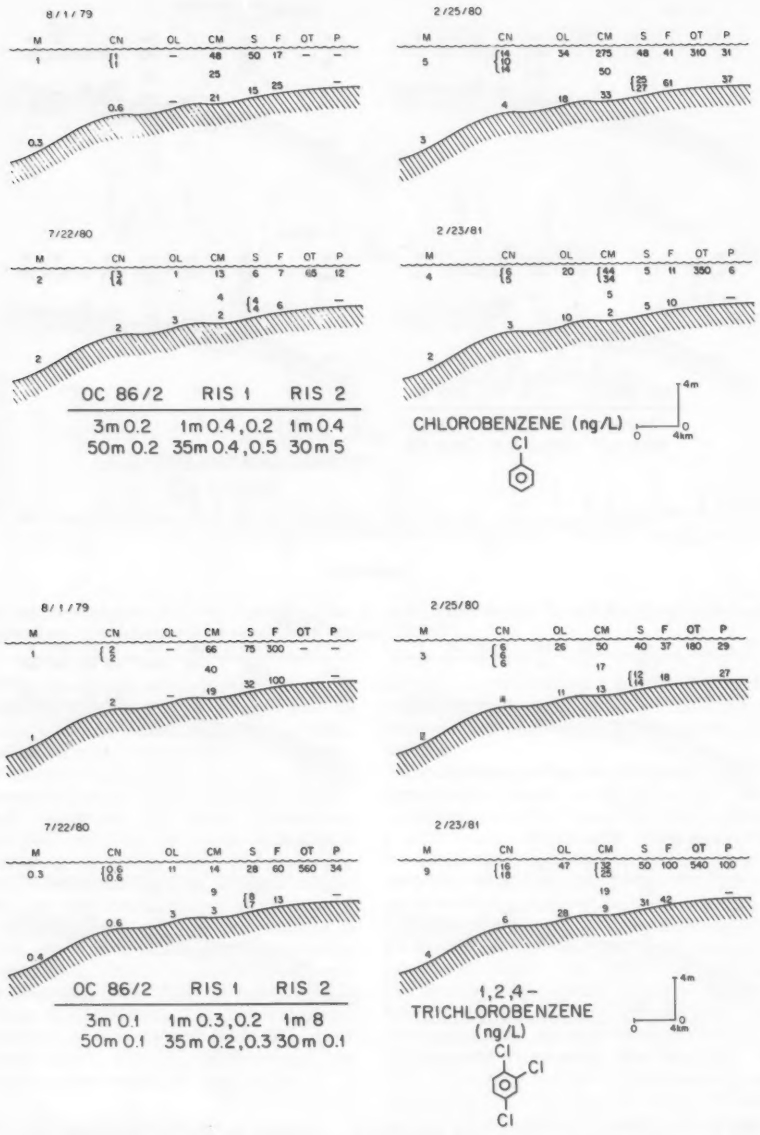

FIG. 6. Chlorobenzene and 1,2,4-trichlorobenzene concentrations (nanograms per litre) in Narragansett Bay. Station locations as for Fig. 5.

concentrations in Rhode Island Sound and at the offshore station are similar to levels of 1–10 ng/L reported in Vineyard Sound (Schwarzenbach et al. 1978; Gschwend et al. 1982) and in northeast Atlantic surface waters (Murray and Riley 1973). Sauer (1981) found trichloroethylene and tetrachloroethylene at 10–50 ng/L in the Gulf of Mexico.

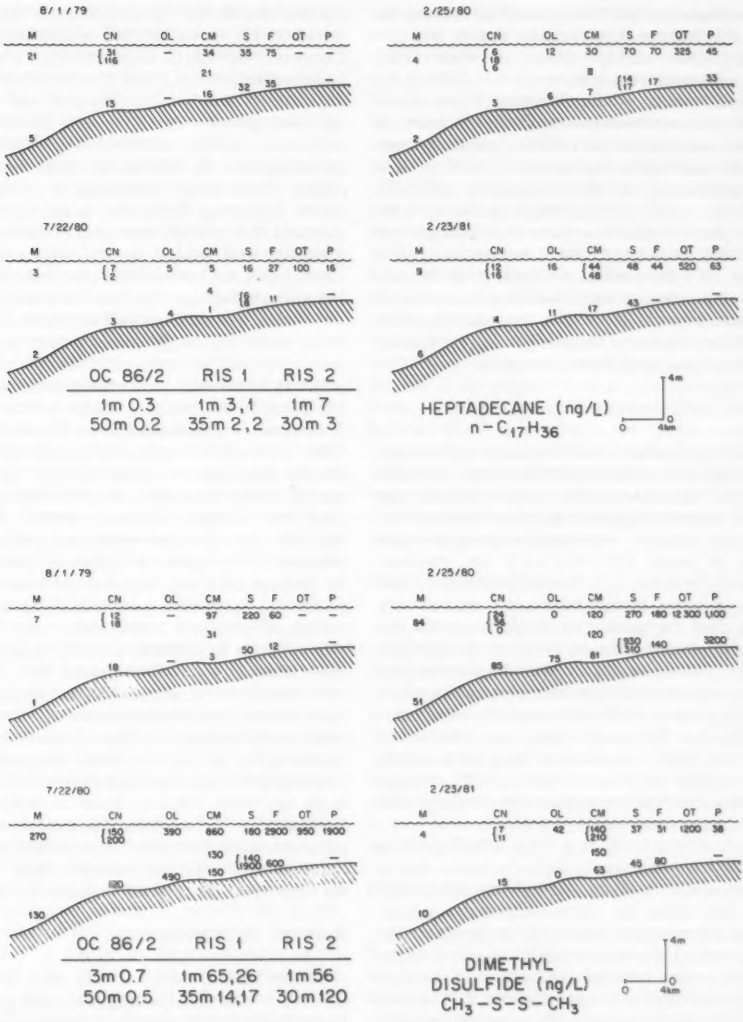

FIG. 7. Heptadecane and dimethyldisulfide concentrations (nanograms per litre) in Narragansett Bay. Station locations as for Fig. 5.

CHLOROBENZENES AND CHLOROTOLUENES

A suite of chlorobenzenes (monochlorobenzenes through trichlorobenzenes) were recovered in most water samples. The dominant chlorinated benzene in the upper bay was usually 1,2,4-trichlorobenzene. The three isomeric chloromethylbenzenes (chlorotoluenes) were also detected in the upper bay samples; 1-chloro-2-methylbenzene dominated. Searches of GC/MS data suggested the presence of dichlorotoluenes and chlorinated naphthalenes in the upper bay, but low levels ($\lesssim$ 1 ng/L) precluded the determination of detailed distributions.

High concentrations of chlorobenzenes and chlorotoluenes at the Fields Point outfall (e.g. Fig. 6) show the sewage effluents to be an important source of these chemicals, again agreeing with industrial uses (USEPA 1980). For chlorobenzene, the winter profiles (Fig. 6) suggest that a second significant source for this compound is probable. The

Pawtuxet River discharges into Narragansett Bay between the Sabin Point and Conimicut Point sampling stations (Fig. 1). Pawtuxet River water collected during the winter 1980 sampling had a chlorobenzene concentration of 2200 ng/L. Inputs of chlorobenzene by the Pawtuxet River would account for elevated concentrations at Conimicut Point. A similar situation was observed for 1-chloro-2-methylbenzene (*o*-chlorotoluene) which had a concentration of 1100 ng/L in the river. Chlorobenzene and chlorotoluene (as well as a variety of other chemicals) have been found previously in the Pawtuxet River and in industrial wastewaters discharged into the river by a small specialties chemical manufacturing plant (Jungclaus et al. 1978; Hites and Lopez-Avila 1980). Significantly lower (1−2 orders of magnitude) concentrations of dichlorobenzenes and trichlorobenzenes were also present in the Pawtuxet River water, and the bay data suggest that the river is not a major source of these compounds.

Aromatic and Alkylaromatic Hydrocarbons

Benzene, toluene, C_2- and C_3-alkylbenzenes, naphthalene, and methylnaphthalenes were consistently found in Narragansett Bay over wide concentration ranges. Benzene and toluene (Fig. 5) were the dominant aromatic hydrocarbons. Individual C_2-alkylbenzenes were present at approximate relative ratios of about 1.4:1.0:3.5:1.9 for ethylbenzene : 1,4-dimethylbenzene : 1,3-dimethylbenzene : 1,2-dimethylbenzene. Relative isomer distributions showed only minor changes along the transect and between summer and winter. Concentrations of 1,3-dimethylbenzene, the dominant isomer, were 5−10 times less than toluene. Naphthalene and C_1-naphthalenes were detected in the bay over a concentration range <1−20 ng/L. In general, concentrations of these aromatic hydrocarbons in Narragansett Bay were considerably higher than the 1−50 ng/L reported in Vineyard Sound by Gschwend et al. (1982) and Mantoura et al. (1982), although relative distributions of these compounds were similar at both locations.

Aromatic hydrocarbon levels (e.g. toluene in Fig. 5) in Narragansett Bay were significantly higher in winter than in summer, a trend similar to chlorinated C_2-hydrocarbons discussed above. But unlike the chloro-compounds, concentration gradients for aromatics were weak, suggesting either uniform inputs around the bay or rapid removal near the sources so as to leave a uniform distribution. The relative abundance of aromatic hydrocarbons in the total VOC assemblage varied both seasonally and with sampling location. In summer, combined aromatic hydrocarbons (toluene + C_2-alkylbenzenes + C_3-alkylbenzenes) were 1−7% of the volatiles in the upper bay compared with 7−37% in the lower bay, while in winter they were 5−30 and 35−70% of the VOC in the upper and lower bay, respectively (see Fig. 2).

In addition to those aromatic hydrocarbons routinely detected in coastal seawater from several locations (i.e. benzene, toluene, C_1- and C_2-alkylbenzenes, naphthalene, and C_1-naphthalenes) (Schwarzenbach et al. 1978; Sauer 1978, 1980, 1981; Gschwend 1979; Gschwend et al. 1980; Gschwend et al. 1982; Mantoura et al. 1982; this report) we found that Narragansett Bay contained significant levels of more highly alkylated aromatic hydrocarbons than has been reported elsewhere. The complexity of these compounds is shown in Fig. 4 via GC/MS specific-ion chromatograms. Compounds through C_5-alkylbenzenes, C_2- and C_3-alkyltetrahydronaphthalenes, C_3- and C_4-alkylindenes, and C_3-alkylnaphthalenes were readily detected, and it is likely that additional groups were also present. No indication as to the relative abundance of each series is given in Fig. 4, since each is normalized to the ion intensity of the most abundant component. However, an examination of ion intensities showed rapidly decreasing abundances as the degree of substitution increased. It is probable that many of these highly substituted aromatics were present in the samples studied by other investigators, but lower overall concentrations compared with Narragansett Bay may have precluded their detection.

Aromatic hydrocarbons probably have multiple sources in Narragansett Bay. High concentrations in the Fields Point outfall area and at Conimicut Point in winter are consistent with uses as industrial solvents and subsequent incorporation into industrial wastewaters. Toluene and the isomeric C_2- and C_3-benzenes were measured in the Pawtuxet River sample at 7900, 6900, and 300 ng/L, respectively. However, industrial solvents are relatively simple mixtures and thus would not account for the complexity observed in the bay. On the other hand, very complex mixtures of aromatic hydrocarbons are relatively abundant in petroleum and petroleum combustion exhausts. Direct inputs via spillage of fuels on the bay or in the drainage basin and from ship and boat traffic on the bay are chronic. Stormwater runoff containing significant concentrations of petroleum hydrocarbons (e.g. Wakeham 1977) may represent an important aromatic hydrocarbon source at many locations around Narragansett Bay. Inputs via stormwater runoff would be periodic and seasonal, with greater inputs during winter when precipitation is greatest. This could then partially account for higher aromatic hydrocarbon concentrations in the bay in winter compared with summer. Direct transfer of aromatic hydrocarbons from the atmosphere to the bay water, either by direct air-to-sea exchange or by dissolution of hydrocarbons into rainfall, may not be very important, since atmospheric concentrations are probably low compared with water concentrations. Rather, exchange from the water to the atmosphere would be favored.

Aliphatic Hydrocarbons

Straight-chained alkanes from nC$_{12}$ to nC$_{18}$, pristane (2,6,10,14-tetramethylpentadecane), and phytane (2,6,10,-14-tetramethylhexadecane) were common constituents of the VOC in Narragansett Bay. Pentadecane and heptadecane were the dominant alkanes. Concentrations were generally low (e.g. heptadecane in Fig. 7) compared with chlorinated C_2-hydrocarbons and aromatic hydrocarbons, and no strong seasonal trends were evident. Levels of about 10 ng/L are comparable with concentrations in Vineyard Sound (Schwarzenbach et al. 1978; Gschwend et al. 1982) but slightly higher than open ocean Gulf of Mexico and Caribbean Sea values of about 1 ng/L for C_6- to C_{14}-alkanes (Sauer 1980, 1981). Numerous cyclic and acyclic C_5- to C_{10}-hydrocarbons were detected in the samples by GC/MS, and these components account for most of the minor peaks in the first halves of the gas chromatograms shown in Fig. 2. It was impossible

to identify most of the low molecular weight alkanes due to the lack of authentic standards. Nevertheless, such a complexity has not been reported previously in seawater, even in samples known to contain petroleum contamination (e.g. Gschwend et al. 1982; Sauer 1980, 1981); again, this may be due to the relatively high levels of VOC in Narragansett Bay making detection of minor components possible.

Odd/even carbon ratios are helpful in distinguishing alkanes of biogenic versus anthropogenic (i.e. fossil) sources. Ratios of $(nC_{15} + nC_{17})/(nC_{14} + nC_{16})$ were 1.3−3 throughout the bay in winter compared with summer values of 2−6 in the upper bay and 3−12 in the lower bay. Ratios near the Fields Point outfall were 1.1−1.7. Values near unity are indicative of petroleum contamination, as would be likely in sewage effluents containing petroleum hydrocarbons from urban runoff (Wakeham 1977; Van Vleet and Quinn 1977, 1978). Higher values ($\gtrsim 3$) indicate an excess of the odd homologs compared with even homologs and suggest a contribution from biogenic sources. None of our samples had odd/even ratios as great as found by Gschwend et al. (1982) in Vineyard Sound (up to 40) during phytoplankton blooms, but our sampling may well have missed blooms. Alkane distributions in Narragansett Bay during summer apparently contain a biogenic component which is relatively greater than a petroleum component, especially in the down-bay region. Concentration variations for duplicate samples, as for example the August 1, 1979, samples at Conanicut Point, are attributed to patchiness of biological production or release of the hydrocarbons to the water. Schwarzenbach et al. (1978), Gschwend et al. (1980), and Gschwend et al. (1982) have discussed phytoplankton and benthic algae as potential alkane sources in coastal areas. In winter, lowered production and release of the biogenic compounds coupled with chronic inputs of petroleum hydrocarbons could lead to odd/even ratios nearer to 1. High levels of heptadecane at the Fields Point Outfall are probably due to petroleum hydrocarbon inputs.

Olefins were only minor components of the hydrocarbon assemblage in Narragansett Bay, a major exception being an incompletely identified octatriene. Concentrations of C_8H_{12} in summer were about 10 ng/L at all locations. However, in winter, levels reached up to 740 ng/L, considerably higher than previously reported in coastal seawater in Vineyard Sound (Gschwend et al. 1982), off Peru (Gschwend et al. 1980), and in Cook Inlet, Alaska (Bates 1980). Gschwend et al. (1982) have tentatively identified the compound as 1,3,5-octatriene and suggest a diatom rather than benthic source. During a diatom bloom in the MERL microcosms, concentrations up to 2500 ng/L were observed for this compound (S. G. Wakeham, unpublished data). High values of the octatriene in Narragansett Bay during late February may correspond to diatom blooms, which occur at this time in the bay, but we have no phytoplankton data to substantiate this suggestion.

Alkylsulfides

As in Vineyard Sound (Schwarzenbach et al. 1978; Gschwend et al. 1982; Mantoura et al. 1982), dimethyldisulfide (CH_3SSCH_3) and dimethyltrisulfide (CH_3SSSCH_3) were present in Narragansett Bay in concentrations fluctuating over a wide range (e.g. dimethyldisulfide in Fig. 7; dimethyldisulfide/dimethyltrisulfide ~3−30). Even in replicate samples, we observed major concentration variations. Nevertheless, in many samples, especially those collected in the summer of 1980, dimethyldisulfide and to a lesser extent dimethyltrisulfide were among the most abundant VOC found (e.g. Fig. 2 and 7). Our method did not detect dimethylsulfide (CH_3SCH_3). Natural production of alkylsulfides has been reported for various microorganisms (Kodata and Ishida 1972; Rasmussen 1974; Banwart and Bremner 1974, 1975, 1976a, 1976b; Jenkins et al. 1967; Zinder et al. 1977; Zinder and Brock 1978) in which the sulfides may be products of the metabolism of sulfur-containing amino acids (e.g. methionine) (Kodata and Ishida 1972). Alternatively, the alkylsulfides may be generated in natural waters by chemical reactions involving methyl mercaptan, itself a microbial product, and in this manner could account for higher alkylsulfide levels in samples stripped a second time, as reported by Schwarzenbach et al. (1978) and Gschwend et al. (1982). High concentrations of dimethyldisulfide and dimethyltrisulfide near the Fields Point Outfall and in upper Narragansett Bay may be due to biogenic production of this compound resulting from degradation of organic matter released to the Bay in the sewage effluents.

Other Compounds

In some samples from the upper bay, we observed significant levels of two isomeric dimethyl-diphenyl-ethers (components 53 and 56 in Fig. 2 tentatively identified as 1-methyl-2-(4-methylphenoxy)benzene and 1-methyl-3-(4-methylphenoxy)benzene ($C_{14}H_{14}O$), respectively). The presence of these compounds was noticed only after automated library searching of GC/MS data. Their major uses are as fragrances for cosmetics and soaps and as heat transfer fluids, so their presence in municipal and industrial sewage effluents is reasonable. Nothing is known about their environmental fates and effects.

Persistance and Fate of VOC in Narragansett Bay

A variety of source and removal processes may influence the distribution of VOC in an estuary, where concentration trends result from a balance between input and removal. Less information is available regarding input rates than removal processes and their predicted rates. Therefore, the discussion that follows will focus on removal processes as they determine the fate and persistence of VOC in Narragansett Bay. The processes considered include dilution with "cleaner" seawater, volatilization, sorption onto particulate matter followed by sedimentation, and degradation (physicochemical and biological). Since VOC cover a range of molecular structures, compound classes may be affected by different processes, and the rates of the processes may vary significantly depending on the type of volatile compound.

Dilution

Dilution of estuary water containing high volatiles levels

TABLE 2. Hydrographic data used to calculate the effect of dilution in Narragansett Bay (complete hydrographic data given in Wakeham et al. 1982b).

	Aug. 1, 1979		Feb. 25, 1980		July 21, 1980		Feb. 23, 1981	
Station	T(°C)	S(‰)	T(°C)	S(‰)	T(°C)	S(‰)	T(°C)	S(‰)
Fields Point								
0 m	26.0	21.6	1.5	26.6	26.3	24.0	4.1	15.0
3 m	—	—	—	—	24.2	26.7	3.6	25.6
5 m	23.3	27.2	1.1	29.5	22.8	28.6	—	—
7 m	—	—	—	—	22.4	29.3	—	—
11 m	—	—	1.1	30.8	20.6	31.1	—	—
Conanicut Point								
0 m	25.5	29.6	1.4	30.3	24.3	31.3	3.2	29.7
3 m	25.3	29.7	—	—	24.1	31.4	3.3	29.4
5 m	22.0	30.0	2.0	31.2	23.9	31.5	3.2	29.4
7 m	20.6	30.2	1.8	31.7	21.1	31.7	—	—
MERL								
0 m	22.5	30.4	—	—	22.3	31.9	3.6	29.0
3 m	22.2	30.4	—	—	21.9	31.9	3.4	29.4
5 m	21.1	30.5	—	—	21.3	31.8	2.7	30.3
7 m	19.3	30.6	—	—	20.7	32.0	2.2	31.0
10 m	19.1	30.6	—	—	19.8	32.1	—	—
13 m	18.8	30.8	—	—	19.6	32.1	—	—

from the head of Narragansett Bay with cleaner water entering the mouth of the bay should result in concentration gradients along the axis of the bay for all components at all times. Such gradients are not observed in all cases (e.g. toluene in summer). Dilution due to tidal flushing alone should reduce the concentration of a conservative property by 50% every 30–50 d (Kremner and Nixon 1978). However, salinity–concentration plots for most volatiles are nonlinear and generally suggest nonconservative behavior along the Fields Point – MERL transect. This may reflect multiple inputs of VOC along the transect or removal processes which act to reduce concentrations faster than would dilution. Concentration decreases often were significantly greater than could be attributed to dilution alone. A simplified mixing model may be derived by proportionally mixing surface water from Fields Point (since many VOC input at the surface from the Fields Point Outfall may be traced along the surface) with water from the MERL station having a mean surface–bottom concentration to give surface water at Conanicut Point using salinity data in Table 2. For tetrachloroethylene, concentrations of about 600 ng/L should be found at Conanicut Point on both August 1, 1979, and February 25, 1980, much higher than the 30 and 40 ng/L, respectively, actually observed (Fig. 5). On the other hand, concentration gradients for toluene were weak, and predicted levels would be 25 and 400 ng/L on these two dates, close to the measured concentrations (Fig. 5). The reason for this difference is that relative abundances of different compound classes (e.g. chlorinated C_2-hydrocarbons vs aromatic hydrocarbons) changed along the axis of the bay in response to processes much more complex than dilution alone.

VOLATILIZATION

Volatilization is probably the major process removing VOC from natural water bodies. Rates of volatilization for nonpolar organic compounds depend on a number of thermodynamic or physicochemical properties such as aqueous solubility, vapor pressure, diffusivity, concentrations of the compound in the water body and in the overlying atmosphere, and the hydrodynamic regime. Since there have been few measurements of volatilization rates in the field, predictive models are important.

Laboratory studies by Dilling and co-workers (Dilling et al. 1975; Dilling et al. 1976) and model calculations by Dilling (1977) and Mackay and co-workers (Mackay and Wolkoff 1973; Mackay and Leinonen 1975; Mackay 1978) suggest that VOC should evaporate from natural water bodies with average mass transfer coefficients (K_L) of ~10 cm/h. However, experiments in the MERL microcosms with a range of chlorinated C_2-hydrocarbons, chlorobenzenes, and aromatic hydrocarbons (Wakeham et al. 1982a) gave mass transfer coefficients of about 0.5–1.5 cm/h, calculated according to eq 4 of Mackay and Leinonen (1975):

$$(1) \quad C_t = C_0 \exp(-K_L t / L)$$

where C_0 is an initial concentration, C_t is a concentration at time t, K_L is the mass transfer coefficient, and L is the 500-cm height of a well-mixed MERL tank. Half-lives ($t_{1/2}$) in the microcosms, calculated as

$$(2) \quad t_{1/2} = 0.69\, L / K_L$$

were 10–30 d, whereas the model of Mackay and co-workers would predict half-lives of a few hours for a 500-cm water column. Mass transfer coefficients of ~1 cm/h have been estimated for 1,4-dichlorobenzene in Lake Zurich (Schwarzenbach et al. 1979) and for alkylbenzenes in Vineyard Sound (Gschwend et al. 1982). Clearly, there is a significant discrepancy between volatilization rates obtained by laboratory studies or predicted by model calculations and

TABLE 3. Calculated mass transfer coefficients (K_L) and residence times (τ) with respect to volatilization for a series of VOC in Narragansett Bay during summer and winter.

	Summer			Winter		
	D^a (10^{-5} cm^2/s)	$K_L{}^b$ (cm/h)	τ^c (h)	D^a (10^{-5} cm^2/s)	$K_L{}^b$ (cm/h)	τ^c (h)
Tetrachloroethylene	0.8	1.9	160	0.4	1.8	170
Chlorobenzene	0.8	1.9	160	0.4	1.8	170
1,4-Dichlorobenzene	0.7	1.7	180	0.3	1.35	220
1,2,4-Trichlorobenzene	0.6	1.4	220	0.3	1.35	220
Toluene	0.8	1.9	160	0.4	1.8	170
1,4-Dimethylbenzene	0.65	1.6	190	0.3	1.35	220
1,3,5-Trimethylbenzene	0.6	1.4	220	0.3	1.35	220
2-Methylnaphthalene	0.6	1.4	220	0.3	1.35	220
n-Dodecane	0.5	1.2	250	0.25	1.1	260
n-Heptadecane	0.4	0.96	310	0.2	0.9	335

[a]Estimated molecular diffusion coefficients during summer (20°C, 30‰) and winter (0°C, 30‰).

[b]Mass transfer coefficient calculated from $K_L = D/z$ (Broecker and Peng 1974) where stagnant boundary film thickness z = 150 μm in summer and 80 μm in winter (z for Narragansett Bay 60–180 μm, Nixon et al. 1980).

[c]Water column residence time with respect to volatilization, $\tau = L/K_L$ where L = 300 cm mean water column mixed depth for Narragansett Bay.

rates measured in microcosms or a lake.

The discrepancy may well lie in the inability of laboratory and model studies to simulate the complexity of hydrodynamic conditions occurring in nature. Cohen et al. (1978) demonstrated in the laboratory that K_L is a complex function of windspeed over a water body and subsequent turbulence. K_L values in nature may vary over several orders of magnitude as the hydrodynamics change over short time scales. Nevertheless, laboratory and model studies show that mass transfer coefficients for a range of VOC having similar solubilities and Henry's Law constants can be quite similar and that even compounds with relatively low water solubilities (e.g. PCBs) may have significant volatilization rates (Mackay and Wolkoff 1973; Mackay and Leinonen 1975).

From our Narragansett Bay data, it is impossible to calculate mass transfer coefficients using eq. 1, since we have no data on concentration changes over time. However, the model of Broecker and Peng (1974) defines a mass transfer coefficient as

$$(3) \quad K_L = D/z$$

where D is the coefficient of molecular diffusion across the liquid–gas interface and z is the interface (hypothetical stagnant boundary layer) thickness. Furthermore, in the bay where inputs of VOC are more or less continuous, it may be more appropriate to consider water column residence times ($\tau = L/K_L$) with respect to volatilization rather than half-lives, which describe "decay" times for non-steady-state situations. We have calculated mass transfer coefficients and residence times for a suite of VOC in summer and winter for Narragansett Bay (Table 3). Molecular diffusion coefficients were estimated by a modified Wilke–Chang equation (Wilke and Chang 1955; Hayduk and Laudie 1974) for summer conditions of 20°C and 30‰ and winter conditions of 0°C and 30‰. Stagnant boundary layer thicknesses of 150 μm in summer and 80 μm in winter were chosen assuming that greater windspeeds in winter might reduce the thickness to a value toward the lower end of the range of 60–180 μm calculated from oxygen exchange measurements by Nixon et al. (1980) for Narragansett Bay, and the reverse in summer. The mass transfer coefficients and residence times in Table 3 must be considered only approximations. Nevertheless, two features are suggested. First, the K_L and τ values are comparable with those of the MERL experiments (where z values of 400–750 μm have been calculated from radon measurements (Bopp et al. 1981)), but they are considerably different from the laboratory and model predictions. And second, if seasonal conditions vary so as to counterbalance D and z, then volatilization rates may be relatively independent of the season. Thus, seasonally variable volatilization rates cannot alone account for the differences in summer vs winter VOC distributions. Catastrophic events such as storms may be the ultimate control on volatilization, not seasonally averaged hydrodynamic conditions.

SORPTION AND SEDIMENTATION

Various investigations (e.g. Chiou et al. 1979; Karickhoff et al. 1979; Means et al. 1980; Schwarzenbach and Westall 1981) have demonstrated that at concentrations typically encountered in natural waters the sorption of nonpolar organic compounds onto natural sorbents is related to the octanol–water partition coefficient of the sorbate and the organic carbon content of the sorbent. For a series of VOC (chlorinated C_2-hydrocarbons, chlorobenzenes, and aromatic hydrocarbons), Schwarzenbach and Westall (1981) and R. P. Schwarzenbach (Swiss Federal Institute for Water Resources and Water Pollution Control, CH-8600, Dubendorf, personal communication), have measured equilibrium partition coefficients ($K_p^x(s)$) in the laboratory for a variety of natural sorbents, including suspended particulate matter and

TABLE 4. Calculated partition coefficients ($K_p^z(s)$) for a series of VOC on Narragansett Bay suspended particulate matter and distribution ($f(s)$) of VOC between particulate and aqueous phases.

Compound	Water solubility[a] (mg/L)	log K_{ow}^z[b]	$K_p^z(s)$[c] (cm_l^3/g_s)	$f(s)$[d]
Tetrachloroethylene	50−400	2.88	22[e]	1.3×10^{-4}
Chlorobenzene	470	2.71	17[e]	1.0×10^{-4}
1,4-Dichlorobenzene	80	3.38	36[e]	2.2×10^{-4}
1,2,4-Trichlorobenzene	20−40	3.60	74[e]	4.4×10^{-4}
Toluene	500	2.58	14	8.4×10^{-5}
1,4-Dimethylbenzene	185	3.5	35[e]	2.1×10^{-4}
1,3,5-Trimethylbenzene	57	3.60	74[e]	4.4×10^{-4}
Naphthalene	32	3.26	42	2.5×10^{-4}
n-Dodecane	3.6×10^{-3}	6.0	4000	2.4×10^{-2}
n-Heptadecane	2.3×10^{-3}	8.5	250000	1.5

[a]Approximate distilled water solubilities at 25°C (McAuliffe 1966; Irman 1965; Eganhouse and Calder 1976; Sutton and Calder 1974, 1975; Hutchinson et al. 1979).

[b]Octanol−water partition coefficients at 25°C, calculated after Leo et al. (1971) or taken from R. P. Schwarzenbach (personal communication).

[c]Equilibrium partition coefficient calculated from $\log K_p^z(s) = 0.72 \log K_{ow}^z + \log f_{oc}(s) + 0.5$ (Schwarzenbach and Westall 1981; R. P. Schwarzenbach (personal communication) where $f_{oc}(s) = 0.06$ determined for a sample of Narragansett Bay suspended particulate matter.

[d]$f(s) = z_{(s)}/z_{(l)}$ or the ratio of compound z on the solid to z in the liquid where $f(s) = (K_p^z(s)\ cm^3/g)/(6 \times 10^{-6}\ g/cm^3)$ for a Narragansett Bay suspended particulate load of 6 mg/L.

[e]R. P. Schwarzenbach (personal communication).

surface sediments from Narragansett Bay. The partition coefficient is defined as

$$(4)\quad S(z) = K_p^z(s)\cdot C(z)$$

with $S(z)$ being the concentration of z on the solid phase ($\mu g/g_s$), $C(z)$ the concentration of z in liquid phase ($\mu g/cm_l^3$), and $K_p^z(s)$ the partition coefficient (cm_l^3/g_s), and may be estimated reliably by

$$(5)\quad \log K_p^z(s) = 0.72 \log K_{ow}^z + \log f_{oc}(s) + 0.5$$

where K_{ow}^z is the octanol−water partition coefficient for z, and $f_{oc}(s)$ is the fractional organic carbon content of the sorbent. Using eq. 4, partition coefficients for a series of VOC on Narragansett Bay suspended matter with a measured organic content of 6% ($f_{oc}(s) = 0.06$) have been calculated and are given in Table 4. Measured values (R. P. Schwarzenbach, personal communication) are in good agreement. However, the solid−water distribution also depends on the availability of solid surfaces for sorption. In Narragansett Bay, the suspended particulate load is about 6 mg/L (Oviatt and Nixon 1975), so that the distribution of compound z between the suspended matter and the water is represented in Table 4 by $f(s)$, the ratio of z on the particulate matter to that in the water. For example, ~0.01% of tetrachloroethylene or toluene should be sorbed onto particulate matter in Narragansett Bay. Even if the suspended material is rapidly turned over in the water column, as during a storm, sorptive losses would still be small, as Gschwend et al. (1982) have calculated for C_2-alkylbenzenes. Only for the alkanes would there be a significant association with particulate matter, and in the case of heptadecane, some 60% would be expected to be sorbed onto the particles in the bay. More of the alkanes could be removed if the particles were deposited and new particles were resuspended. Therefore, except for the alkanes, sorption of VOC should not be important in Narragansett Bay, and removal to the sediments of most VOC should be minimal.

DEGRADATION

Degradation of VOC in estuarine seawater could involve a combination of processes: hydrolysis, photolysis, oxidation, and biodegradation. Little information is available concerning hydrolysis or photolysis of VOC under environmental conditions, but neither process is expected to be important. Mabey and Mill (1978) estimate hydrolysis half-lives of hundreds of years for polyhalogenated methanes, although hydrolysis of monohalogenated alkanes may be faster. Dilling et al. (1975) carried out laboratory experiments to assess hydrolysis of chloroform, trichloroethylene, and tetrachloroethylene and found half-lives of 9−15 mo. Information pertaining to environmental hydrolysis of aromatic hydrocarbons and halogenated aromatic hydrocarbons has not been found, but such reactions are unlikely (Callahan et al. 1979). Photolysis and oxidation of VOC in the aquatic environment under ambient conditions are also poorly understood but probably are not significant in most cases (Callahan et al. 1979). Possible exceptions are trichloroethylene and tetrachloroethylene which are photooxidized in aqueous medium in sunlight

(Dilling et al. 1975). Oxidation in the atmosphere does appear to play an important role for many VOC once they are volatilized from the water body (Callahan et al. 1979).

Biologically mediated degradative processes are better understood for VOC. Bouwer et al. (1981) found in the laboratory that trihalomethanes, trichloroethylene, and tetrachloroethylene were not significantly degraded under aerobic conditions by bacterial inocula from sewage effluents. Oxidation of monohalogenated benzenes by soil bacteria is slow unless in the presence of other substrates (e.g. toluene) acting as carbon sources, in which case degradation is enhanced (Gibson et al. 1968). More than one halogen atom on the aromatic nucleus greatly reduces biodegradation rates, although soil microbes will still slowly degrade dichlorobenzenes (Ballschmiter and Scholz 1980) and trichlorobenzenes (Marinucci and Bartha 1979). Biodegradation of aliphatic and aromatic hydrocarbons has recently been reviewed by Jordan and Payne (1980). In general, degradation rates of volatile hydrocarbons can be fast but vary greatly depending on environmental conditions, especially temperature and the abundance of hydrocarbon-degrading populations.

MERL experiments (Gearing et al. 1979; Gearing and Gearing 1982a, 1982b; Wakeham et al. 1982a) suggest that conditions in an ecosystem like Narragansett Bay can be conducive to rapid biodegradation of some VOC, particularly aromatic hydrocarbons and chlorobenzene. Wakeham et al. (1982a; unpublished data) found that once degradation commenced, usually after an induction period, concentrations of aromatic hydrocarbons and chlorobenzene could be reduced by 2–4 orders of magnitude in 12–24 h. Aliphatic hydrocarbons apparently were degraded less rapidly. The experimental data were insufficient to allow for detailed determinations of winter vs summer degradation rates. However, in summer, the induction period appeared to be shorter, suggesting that populations capable of degrading these compounds were either more abundant initially or became acclimated to the chemicals more rapidly in the warmer water case or that metabolism was faster at the warmer temperature. Chlorinated C_2-hydrocarbons, dichlorobenzenes, and trichlorobenzenes appeared to be unaffected by biodegradation in the microcosms.

Thus, extensive and rapid biodegradation of aromatic hydrocarbons in Narragansett Bay could help to explain the very low concentrations for these compounds found in summer and the absence of major concentration gradients during both summer and winter (e.g. Fig. 6). Previous investigators (Grob and Grob 1974; Gschwend et al. 1982) have reported rapid depletions of ethylbenzene and *n*-propylbenzene relative to their isomers and attributed such isomer ratio changes to preferential biodegradation of the more vulnerable isomer. Neither our bay measurements nor our MERL experiments have shown such isomeric discriminations, but this could be due to the relatively high concentrations with which we are dealing. If chlorinated C_2-hydrocarbons and chlorobenzenes are not readily degraded in the bay, then some other removal process, primarily volatilization, must play a major role in the observed concentration changes along the sampling transect.

Acknowledgments

We thank J. L. Lake, M. A. McGregor, and B. W. Tripp for assistance in collecting the water samples. M. A. McGregor, J. W. Farrington, R. P. Schwarzenbach, P. M. Gschwend, and J. K. Whelan provided valuable discussions regarding the data and their interpretation and on the manuscript. R. F. Bopp provided the estimated molecular diffusion coefficients, R. P. Schwarzenbach determined sorption coefficients on Narragansett Bay particulate material, and N. M. Frew assisted in gas chromatography – mass spectrometry. This research was supported by United States Environmental Protection Agency grants R80607212 and CR807795 to the Marine Ecosystems Research Laboratory, University of Rhode Island.

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A Large-Volume Sampling Assembly for the Determination of Synthetic Organic and Petroleum Compounds in the Dissolved and Particulate Phases of Seawater[1]

B. W. DE LAPPE, R. W. RISEBROUGH, AND W. WALKER II

Bodega Marine Laboratory, University of California, Bodega Bay, CA 94923, USA

DE LAPPE, B. W., R. W. RISEBROUGH, AND W. WALKER II. 1983. A large-volume sampling assembly for the determination of synthetic organic and petroleum compounds in the dissolved and particulate phases of seawater. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 322–336.

A system for the in situ sampling of subsurface seawater for the determination of synthetic organic and petroleum compounds in concentrations of picograms per litre is described. Seawater from in front of the bow of the vessel was pumped through a stainless steel tube into a cleanroom, through a glass fiber filter, and through parallel or serial Teflon® columns packed with a porous polyurethane foam (PPF) solid adsorbent. The majority of hydrocarbons associated with seawater particles were quantitatively recovered. The efficiency of the foam columns in extracting the dissolved phase was determined by intercalibration with liquid–liquid extraction using cyclohexane and by separate analyses of two columns mounted in series. Recovery of polychlorinated biphenyls, several chlorinated hydrocarbon biocides, and aromatic hydrocarbons was quantitative with a single PPF column. Measured concentrations were in the low picogram per litre range for chlorinated organics and the nanogram per litre range for total petroleum. Reduction of contamination during sampling remains of paramount importance in the determination of hydrocarbon concentrations in seawater.

DE LAPPE, B. W., R. W. RISEBROUGH, AND W. WALKER II. 1983. A large-volume sampling assembly for the determination of synthetic organic and petroleum compounds in the dissolved and particulate phases of seawater. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 322–336.

Nous décrivons dans l'article qui suit un système d'échantillonnage in situ d'eau de mer sous la surface, en vue de déterminer les composés organiques synthétiques et de pétrole à des concentrations de picogrammes par litre. L'eau de mer a été pompée à l'avant d'un bateau, passant par un tube en acier inoxydable à un endroit propre, et traversant un filtre en fibre de verre et des colonnes de Teflon® en parallèle ou en série et bourrées d'un absorbant solide poreux de polyuréthane mousse (PPF). La plus grande partie des hydrocarbures associées aux particules dans l'eau de mer ont été quantitativement récupérées. Le rendement des colonnes de mousse dans l'extraction de la phase dissoute a été déterminé par intercalibrage dans une extraction liquide–liquide au cyclohexane et par analyses séparées des deux colonnes montées en série. Avec une seule colonne de PPF, la récupération des BPC, de plusieurs bioxydes d'hydrocarbures chlorés et d'hydrocarbures aromatiques est quantitative. Les concentrations mesurées sont comprises dans un étroit éventail de picogrammes par litre pour les composés organiques chlorés et nanogrammes par litre pour le pétrole total. Une contamination aussi basse que possible au cours de l'échantillonnage demeure d'une grande importance dans la détermination des concentrations d'hydrocarbures dans l'eau de mer.

Received March 19, 1982
Accepted November 29, 1982

Reçu le 19 mars 1982
Accepté le 29 novembre 1982

THIS paper describes a large-volume seawater sampling assembly used in the determination of concentrations of synthetic organic and petroleum compounds in both the dissolved and particulate phases of seawater. The development of this sampling equipment was guided by the experience acquired in previous programs (Osterroht 1974; Dawson et al. 1976; Risebrough et al. 1976; Green 1978; de Lappe et al. 1980). Previously we described the construction and application of a modified Bodman sampler (the Bodega–Bodman) (de Lappe et al. 1980) which collected 90-L samples at depths throughout the water column to within 10 m above the bottom. These samples were expensive to collect and transport to the laboratory, difficulties were encountered in reducing contamination during sampling, and sample sizes of 90 L were frequently insufficient for detailed chemical studies. These factors

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6871)
Imprimé au Canada (J6871)

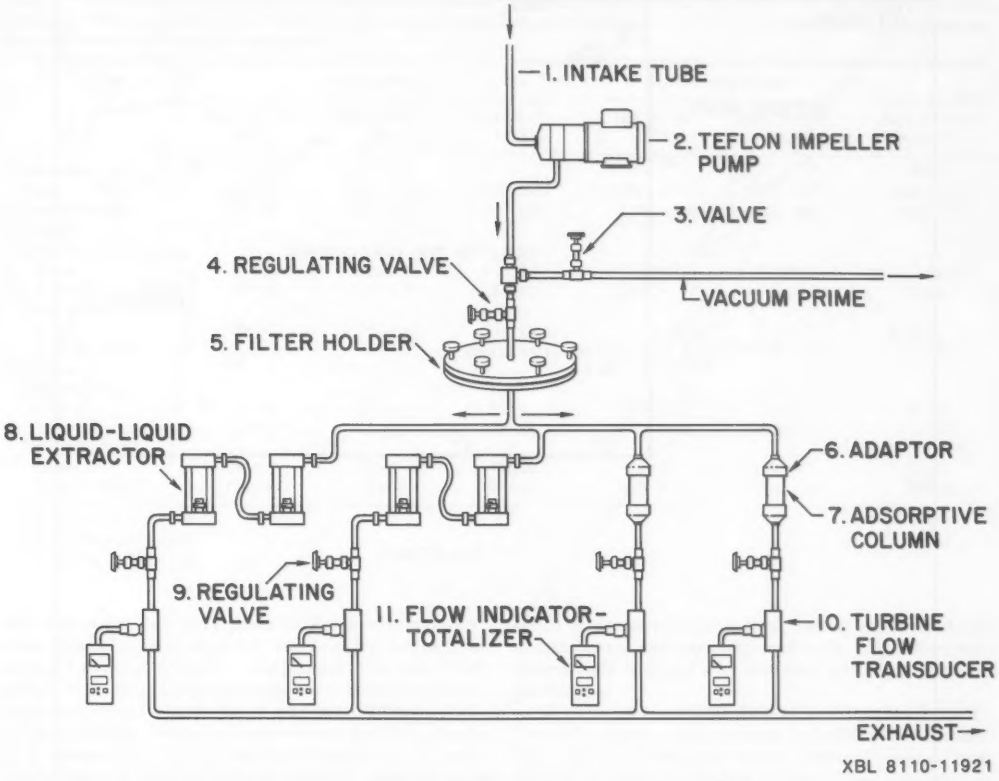

FIG. 1. Shipboard trace organic filtration–extraction system: PPF adsorptive columns and liquid–liquid extractors.

prompted the development of systems which extract seawater in situ through the use of a solid adsorbent (Osterroht 1974). Adsorbents employed have included both XAD macroreticular resins (Harvey 1973; Harvey et al. 1973; Musty and Nickless 1974a; Osterroht 1974) and porous polyurethane foam (PPF) (Uthe et al. 1972; Musty and Nickless 1974b; Musty and Nickless 1976; Carmignani and Bennett 1976). We have used the Slocum sampler, which consisted of a stainless steel column packed with PPF plugs (Risebrough et al. 1976). This sampler was suspended to depths of approximately 3 m; a shipboard vacuum system brought water through the column and a length of vacuum tubing for determinations of volume onboard ship. A modification of this system (de Lappe et al. 1980) provided for the separate collection of a particulate fraction on a glass fiber filter mounted in front of the PPF column.

Additional modifications to the Slocum sampler are described in this paper. These were designed to (1) reduce the possibility of contamination by placing the entire sampling assembly in a shipboard cleanroom, (2) permit replacement of the filter whenever sampling load reduced flow rate, thereby increasing the sampled water volume, (3) provide for intercalibration with other extraction systems, and (4) provide estimates of recovery efficiencies.

Materials and Methods

Components of sampling assemblies (Fig. 1) were washed with soap and water, followed by successive rinses of methanol, acetone, and hexane (Burdick & Jackson). A final hexane rinse was reduced to approximately 1 mL and analyzed by gas chromatography (GC) using both a flame ionization detector (FIDGC) and an electron capture detector (ECGC). This process was repeated until no peaks eluting after n-C_{15} were present that could represent 1 pg/L of an individual organochlorine compound, or 1 ng/L of an individual nonchlorinated hydrocarbon, in a 1000-L sample of seawater. The glass fiber filters were kiln-fired overnight at 500°C and wrapped in solvent-rinsed aluminum foil, which had also been kiln-fired, for transport to the field.

Molded Teflon® tubing (30.5 cm long, 6.35 cm outside diameter, 5.08 cm inside diameter) was fashioned into columns, and these were packed with five PPF plugs (United Foam Corp., Hayward, CA; density 0.0285 g/cm^3; product

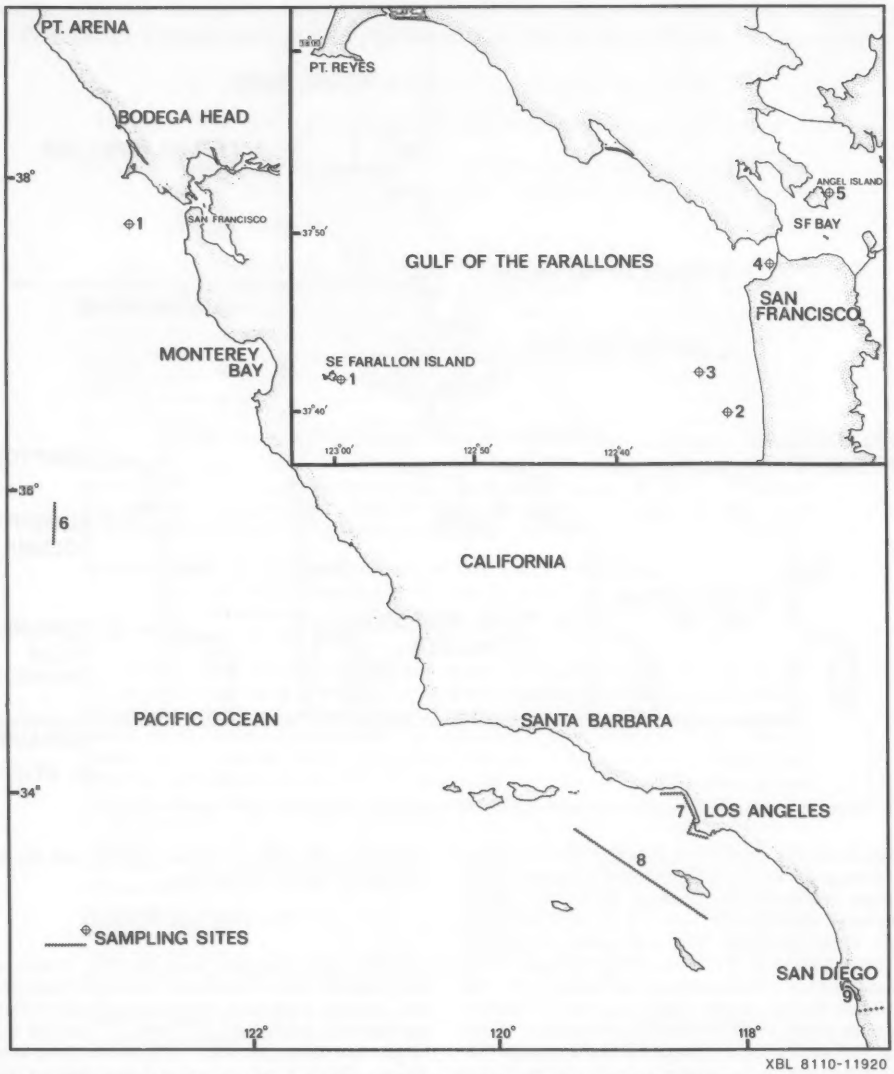

FIG. 2. Sampling sites: 1, Southeast Farallon Island; 2, Pacifica; 3, South San Francisco; 4, Golden Gate Channel; 5, San Francisco Bay; 6, Eastern Pacific Ocean; 7, Coastal Los Angeles; 8, Outer Santa Barbara Passage; 9, San Diego Harbor.

No. 2079). The foam plugs were extracted with acetone in a large Soxhlet apparatus for a minimum of 72 h before packing, and packed columns were rinsed with cold acetone and hexane (Burdick & Jackson). A final hexane rinse was reduced to a small volume by rotary evaporation for GC analysis. This procedure was repeated until satisfactory blanks (see above) were obtained. Columns were primed for seawater sampling with a final 500-mL methanol rinse and sealed in Teflon® bags for transport to the field.

The research vessel *Invincible*, an 11-m fiber glass motorsailor, was the sampling platform. Sampling sites are shown in Fig. 2. The seawater intake tube for anchored stations consisted of two 3-m segments of $\frac{3}{4}$-in. stainless steel tubing coupled to a 1.5-m length of $\frac{3}{4}$-in. Teflon® pipe at the point of attachment to the hull. The intake tube collected water from a depth of 1−2 m and was supported off the bow of the vessel

TABLE 1. Intercalibration of extraction efficiencies of hydrocarbons (boiling range between n-C_{14} and n-C_{35}) from the dissolved phase of seawater by PPF columns and liquid–liquid (cyclohexane) extractors. Data represent means ± SD (N = 2) of concentrations (nanograms per litre) uncorrected for recovery or background.

	Goleta Point[a]			San Nicholas Island[b]		Corona del Mar,[c]
	Aug. 25–26, 1978	Sept. 3–4, 1978	Sept. 4–5, 1978	Sept. 9–10, 1978	Sept. 10–11, 1978	Sept. 14–15, 1978
Volumes (L)						
Foam	1143, 379	1304, 1349	1260, 1474	1491, 1354	1333, 1275	1406, 1253
Liquid–liquid	90, 87	121, 123	133, 115	137, 136	132, 125	103, 125
Saturates						
Total resolved						
Foam	20±24	3.3±0.6	1.3±1.5	2.9±0.1	3.7±0.5	2.1±0.6
Liquid–liquid	30±20	3.5±1.7	26±10	5.0(N = 1)	4.3(N = 1)	12±0.7
Total unresolved						
Foam	100±81	19±8	5.6±1.1	1.7±0.3	2.3±0.2	0.72±0.29
Liquid–liquid	120±14	32±16	73±4	4.0(N = 1)	2.5(N = 1)	9.3±0.1
Aromatics						
Total resolved						
Foam	57±34	23±1	11±4	5.3±2.8	2.7±0.1	12±0
Liquid–liquid	21±13	11±8	27±21	4.4(N = 1)	5.3(N = 1)	6.2±6.8
Total unresolved						
Foam	190±78	59±9	30±10	11±3	6.8±2	33±4
Liquid–liquid	120±44	75±35	65±33	34(N = 1)	25(N = 1)	43±16

[a]34°24.1′N, 119°50.5′W.
[b]33°13.0′N, 119°29.0′W.
[c]33°34.7′N, 117°51.7′W.

with a spinnaker pole and topping lift. For moving transects, water was collected through ¾-in. stainless steel tubing from a point 1 m below the surface and forward of the bow of the vessel. In the field, equipment subjected to possible contamination was rinsed with methanol, acetone, and hexane.

The plumbing system employed permits the PPF columns to be mounted in series, in parallel (shown in Fig. 1), or in combination. A noncontaminating Teflon® impeller pump (Jupiter, Fluorocarbon Corp.) pumps seawater through a glass fiber filter with a rated pore size of 0.3 μm (type A/E, Gelman Corp.). The filtrate was split to pass through either PPF columns or two-stage liquid–liquid extraction units constructed in the design of Ahnoff and Josefsson (1974). Cyclohexane was used in the liquid–liquid extractors. Flow rates and total volume passing through the foam sorption and liquid–liquid extractors were individually monitored with turbine flow meters (Omni-Flo, Flow Technology, Inc., Phoenix, AZ). Flow rates were controlled with regulating valves downstream from the extractors. Rates were approximately 100 mL/min for the liquid–liquid extractors. PPF extraction rates varied but typically were about 1000 mL/min.

Filters were changed whenever flow rates dropped below 50% of normal. At stations in bays and harbors, suspended particulate load necessitated filter changes as frequently as every 2 h. Sample collection throughout a 25-h period resulted in obtaining a composite sample over a complete tidal cycle. Filters and columns were resealed in Teflon® bags and frozen immediately after sampling; cyclohexane from the liquid–liquid extractions was also stored in the shipboard freezer.

Blanks consisted of packed columns in Teflon® bags, which were transported to the field, opened, and resealed, and of cyclohexane that was transported to the field. These were subsequently analyzed with the same procedures used for the samples.

All glassware used in the analyses was kiln-fired at 500°C. The PPF columns were extracted with 500 mL of acetone, followed by 500 mL of hexane. Solvent volumes were reduced by rotary evaporation, combined, and partitioned in a 2-L separatory funnel with 700 mL of purified water to remove the acetone; the organics were collected in the hexane layer. The acetone–water mixture was back-extracted once with an additional 300-mL hexane extract of the foam column. The combined hexane extractions were reduced to approximately 2 mL prior to column chromatography. The cyclohexane of the liquid–liquid extractors was reduced by rotary evaporation and dried by passage through sodium sulfate (Mallinckrodt; kiln-fired before use) prior to column chromatography. Particulate filters were torn into 1-cm^2 pieces with stainless steel tweezers and placed in a 2-L round-bottom flask. They were refluxed for 12 h using two 12-h extractions with 750 mL of acetone, followed by two 12-h extractions with 750 mL of hexane.

Column chromatographic separations of samples from the Southern California Bight collected in 1978 were done using Alcoa alumina F-20, 80/100 mesh, and Hi-Flosil silica gel, 60/200 mesh (Applied Science Laboratories). Column chromatographic separations of the samples obtained after 1978 were done using Florisil. The silica and alumina were cleaned with methanol rinses before overnight activation at 240°C. Columns were prepared to a length to diameter ratio of 20:1 with two parts of silica underneath one part of alumina by weight such that the weight of the alumina exceeded 100 times

TABLE 2. Intercalibration of extraction efficiencies of selected hydrocarbons from the dissolved phase of seawater by single PPF columns and liquid–liquid (cyclohexane) extractors ($N = 2$) compared with concentrations in the particulate phase. Data represent means ± SD uncorrected for recovery or background.

	Golden Gate Channel,[a] Nov. 5–6, 1978	South San Francisco,[b] Nov. 2–3, 1978	Pacifica,[c] Nov. 1–2, 1978	Southeast Farallon Island,[d] Oct. 27–28, 1978
Volumes (L)				
Foam	990, 950	1259, 1106	1121, 1121	1519, 1626
Liquid–liquid	106, 101	114, 106	116, 118	173, 159
PCBs (pg/L)				
Foam	160±57	130($N = 1$)	74±14	18±2
Liquid–liquid	145±21	71±3	63±18	28±4
Particles	260	150	98	—
p,p'-DDE (pg/L)				
Foam	9±0.6	8($N = 1$)	6±3	2.6±2.0
Liquid–liquid	19±3	11±1	9±3	8.6±3.4
Particles	18	10	8	—
p,p'-DDT (pg/L)				
Foam	4.8±0.3	5.2±1.8	7.8±0.9	4.9±1.1
Liquid–liquid	31±21	<10	12±3	5±0.5
Particles	36	21	14	—
α-Chlordane (pg/L)				
Foam	23±0	15±2	11±2	16±2
Liquid–liquid	36±10	14±3	15±2	17±1
Particles	16	8	7	—
α-HCH (pg/L)				
Foam	46±3	40±7	47±0.7	31±10
Liquid–liquid	220±20	140±7	160±0	130±21
Particles	4	2	<2	—
Unresolved components (ng/L)[e]				
Foam	60±9	25($N = 1$)	31±6	6.4±0.4
Liquid–liquid	340±130	170±19	190±15	120±14
Particles	1400	610	220	9[f]

[a]37°47.75′N, 122°29.45′W.
[b]37°42.13′N, 122°34.45′W.
[c]37°40.00′N, 122°32.25′W.
[d]37°41.80′N, 122°59.80′W.
[e]Sum of both saturated and aromatic compounds.
[f]November 7–8, 1978.

the weight of the sample lipid. Sample extracts applied to chromatography columns in 2–3 mL of hexane were eluted successively with hexane and benzene. Florisil (Supelco, 60/100 mesh) was activated at 250°C for 12–15 h, placed in a desiccator until cool, deactivated with 0.5% H_2O, stored in a sealed container in a desiccator overnight, and then used within 72 h. Columns were rinsed with hexane. Samples extracts were applied to the columns in 2–3 mL of hexane. Sufficient hexane to elute the polychlorinated biphenyls (PCBs) and *p,p'*-DDE, but not *p,p'*-DDT, was added and collected as fraction I. Sufficient 30% methylene chloride in hexane (v/v) to elute *p,p'*-DDT and α- and γ-chlordane, but not dieldrin, was added and collected as fraction II. Sufficient 50% methylene chloride in hexane (v/v) to elute all dieldrin and endrin was added and collected as fraction III.

FIDGC was accomplished using Hewlett-Packard 5840A gas chromatographs equipped with automatic liquid sampler injectors and Grob-type capillary inlet systems. Prior to 1980, AA grade efficiency 30-m glass capillary columns (J & W Scientific), rated at a minimum of 2500 effective plates per meter, were used for all analyses. Aliphatic (saturated) fractions were analyzed using a nonpolar SP-2100 phase column, while aromatic fractions were analyzed using a more polar SE-54 phase. Analyses after 1980 used fused silica capillary columns (J & W Scientific), an SE-30 for the aliphatic (saturated) fractions, and an SE-54 for the aromatic fractions. All FIDGC injections were made in the splitless mode at an initial temperature of 50°C. The inlet was purged after 1 min, and the oven temperature was increased at 10°/min to 100°C and then at a rate of 3.5°/min to a maximum temperature of 270°C using glass capillary columns and 280°C with fused silica columns. The carrier gas was helium.

Areas of the unresolved complex mixtures (UCM) were measured by planimetry. The concentrations of the UCM were determined either on the basis of the mean response per nanogram of the alkanes within the range of the UCM or on the basis of the response per nanogram of a single alkane, n-C_{23}, in an external standard run each day. The results obtained by these two methods were equivalent (Risebrough et al. 1983); they were also equivalent to those obtained by the

TABLE 3. Concentrations of hydrocarbons in the particulate phase of 1270 L of seawater, and recovery of hydrocarbons from the dissolved phase by two PPF columns mounted in series (expressed as picograms per litre of seawater; San Francisco Bay near Angel Island, August 3–4, 1980).

		Dissolved phase		
	Particles (pg/L)	First column (pg/L)	Second column	
			pg/L	% of first
Total resolved (saturates)	150 000	9 100	3700	41
Total unresolved (saturates)	1 600 000	57 000	5000	9
n-C_{15}	5 600	210	120	57
n-C_{17}	4 200	570	90	16
Pristane	2 700	180	60	33
n-C_{18}	1 200	460	40	9
Phytane	1 900	140	20	<14
n-C_{29}	14 000	150	10	<7
Total resolved (aromatics)	120 000	22 000	1200	5
Total unresolved (aromatics)	160 000	34 000	5200	15
Phenanthrene	1 300	1 900	<50	<3
Anthracene	350	150	<50	<33
Pyrene	4 000	1 600	<50	<3
Squalene	7 700	<50	<50	—
Heneicosahexaene	36 000	<50	<50	—
PCB	440	220	4	2
p,p'-DDE	26	35	0.4	1
p,p'-DDD	66	45	0.6	1
p,p'-DDT	29	3.7	0.4	11
α-HCH	9	430	200	47
β-HCH	<5	340	110	32
γ-HCH	3.9	200	120	60
γ-Chlordane	90	26	1.3	5
α-Chlordane	11	29	0.4	1.3
trans-Nonachlor	18	27	<0.1	<0.4
Dieldrin	9	153	—	—
Endosulfan I	<1	29	—	—

methodologies used in other laboratories (W. B. Galloway, USEPA, Narragansett, RI 02882, personal communication).

ECGC was accomplished using a Carlo Erba 2150 gas chromatograph with a ^{63}Ni Brechbuhler microelectron capture detector. Injections were made in a split mode at an initial oven temperature of 140°C. The oven temperature was increased at a rate of 3.5°/min to a maximum temperature of 275°C. Both SE-30 and SE-54 fused silica columns were used. A known amount of decachlorobiphenyl (DCB) was coinjected as an internal standard with all capillary ECGC runs. Inlet and detector temperatures were maintained at 250 and 255°C, respectively. The carrier gas was helium, and argon containing 10% methane purged the electron capture detector.

Peaks on electron capture chromatograms that could be identified were quantified on the basis of the internal standard and corrected for the relative response of an authentic standard to that of DCB. Toxaphene was quantified by a comparison of both the areas of peaks and unresolved components with those of a toxaphene standard.

Mass spectrometric (MS) analyses of selected extracts were done on a modified Finnigan 4023 mass spectrometer and Incos data system. A 30 m × 0.318 mm fused silica open tubular capillary column coated with DB5 liquid phase of a 0.25-μm film thickness (J & W Scientific) was used. The carrier gas was helium. Splitless injection was used for all samples; the outlet of the column was connected so that the total column effluent, between 1 and 2 mL/min, entered the ion source directly. Temperatures used were as follows: injector, 290°C; transfer oven, 285°C; MS manifold, 125°C; ion source, 250°C. The column oven temperature was held by means of liquid nitrogen at 45°C for 3 min, during which the injection was accomplished, and then elevated to 300°C at 4°C/min. The oven remained at 300°C until the end of each analysis. The quadrupole mass filter was scanned from M/z 36 to M/z 536 in 1 s with centroid sampling at 200-ms intervals; the sample examined for toxaphene was analyzed such that the quadrupole passed ions at M/z 125, 161, 197, 245, and 271, all $\pm 0.5\ M/z$. The conversion dynode was held at −2.8 kV, and a continuous dynode electron multiplier was operated at 1.1 kV.

Results and Discussion

In the approach to the present study, sampling variance associated with patchiness in the distribution of hydrocarbons in seawater was reduced by continuous sampling during a complete tidal cycle. An indication of local variability is provided by three samplings at Goleta Point, the site of an active oil seep on the Southern California coast, and two samplings at San Nicholas Island in the outer Southern California Bight (Table 1). Measured concentrations of total

TABLE 4. Concentrations of hydrocarbons in the particulate phase of seawater, and recovery from the dissolved phase by PPF columns mounted in parallel and in series (expressed as picograms per litre; Southern California Bight, transect between 33°09′N, 118°20.5′W and 33°46.5′N, 119°23.0′W, October 16–17, 1980).

		Columns in series		
	Column A	First	Second	Particles
Volume (L)	1398	1116		2 514
Total resolved (saturates)	<1100	<1 900	<1900	75 000
Total unresolved (saturates)	<8300	<10 000	<7800	21 000
Total resolved (aromatics)	4200	2 400	1600	37 000
Total unresolved (aromatics)	<9800	<4 500	<7800	<3 800
PCB	2.9	2.4	0.2	2.3
p,p′-DDE	15	18	0.1	4.7
o,p′-DDE	8	6	<0.5	<1
p,p′-DDD	7	13	<0.5	4.7
p,p′-DDT	1.0	1.7	<0.5	4.5
α-HCH	>80	260	40	<10
γ-Chlordane	7	11	<0.5	<1
α-Chlordane	8	12	<0.5	<1
trans-Nonachlor	5	9	<0.5	<1

TABLE 5. Concentration of hydrocarbons in the particulate phase of seawater, and recovery from the dissolved phase by PPF columns mounted in parallel and in series (expressed as picograms per litre; Eastern Pacific Ocean, transect between 35°55′N, 123°35′W and 35°38′N, 123°34′W, September 28–29, 1980).

		Columns in series		
	Column A	First	Second	Particles
Volume (L)	2273	1988		4 261
Total resolved (saturates)	<1400	<1300	<820	12 000
Total unresolved (saturates)	<2500	<4000	<4000	<12 000
n-C_{15}	<290	<280	<110	2 900
n-C_{17}	<40	<23	<23	280
Pristane	<23	<14	<11	330
Total resolved (aromatics)	2500	2800	730	54 000
Total unresolved (aromatics)	<2500	<5000	<2300	<10 000
PCB	<0.3	<2.8	<2.1	<0.9
p,p′-DDE	<0.02	<0.3	<0.8	<0.3
Toxaphene	48	55	<1	<1
α-HCH	—	290[a]	160	<0.2

[a]Quantified by GC/MS.

hydrocarbons were equivalent in the two samples obtained from San Nicholas Island, but one of the three samples from Goleta Point yielded values several times higher than those of the other two.

A measure of analytical variability is provided by comparisons of the values obtained from two PPF columns or two liquid–liquid extraction units mounted in parallel (Tables 1, 2, 4, 5). Contributing to the analytical variance are the losses incurred in reducing volumes of many of the final extracts. In addition to these sources of variation, the measured concentrations of hydrocarbons in seawater might be either (1) too high because of contamination during sampling or analysis or (2) too low because of incomplete recovery.

DETERMINATION OF THE BACKGROUND

The recent history of the measurements of both metals (Patterson et al. 1976; Martin et al. 1976; Bruland et al. 1978) and organic pollutants (de Lappe et al. 1980) in seawater indicates that many early determinations were probably too high due to contamination during sampling and/or difficulty in establishing "blank" or background values. In the present study, contamination was reduced by the design and extensive cleaning of sampling equipment as well as through precautions undertaken during sampling. In addition, increasing the volume of seawater sampled diluted contamination from sources not associated with the seawater. These procedures have resulted in determinations in the dissolved phase of a number of chlorinated compounds in the low picogram per litre range (Tables 2–5), and of total hydrocarbons, within a boiling range of the alkanes *n*-C_{14} and *n*-C_{35}, of 10–100 ng/L in the dissolved phase (Tables 1, 5).

Laboratory checks and the analysis of field blanks showed very few contaminants. *p,p′*-DDE, *p,p′*-DDT, homologous

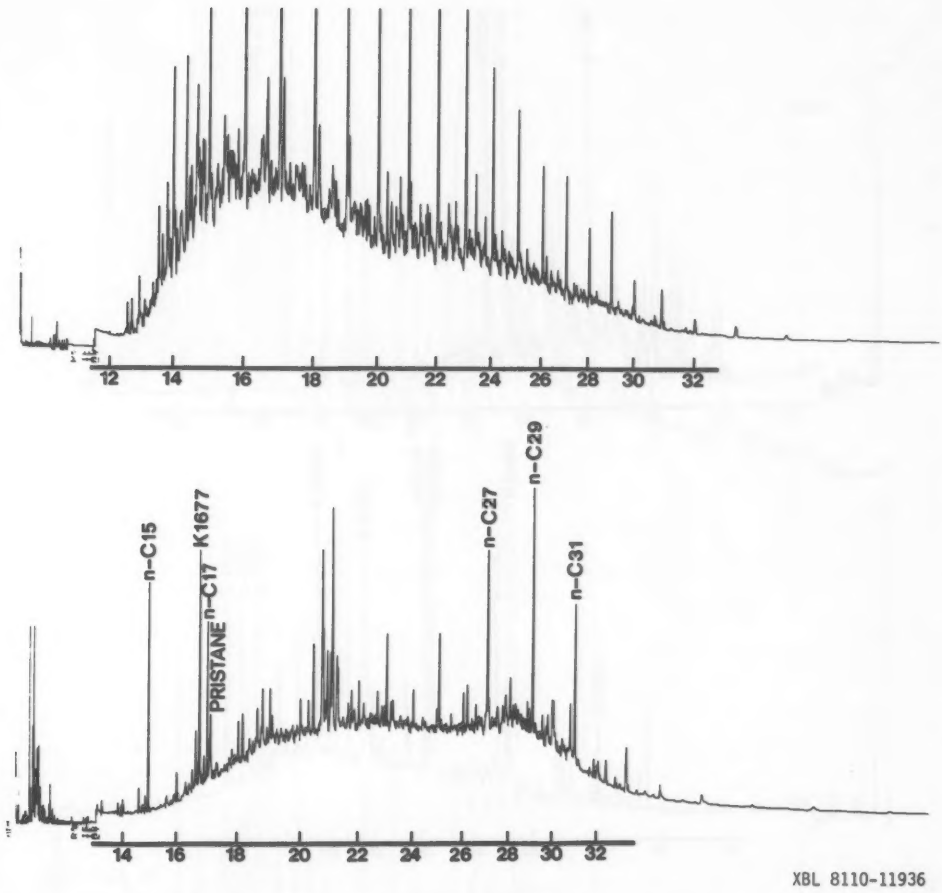

FIG. 3. FID chromatograms of saturated fractions of dissolved (top) and particulate (bottom) phases of seawater sampled in the vicinity of Angel Island, San Francisco Bay, August 3–4, 1980 (1270 L). Numbers represent the emergence times of the *n*-alkanes. Gas chromatographic conditions are described in the text.

series of *n*-alkanes, and the unresolved component of the saturated fraction could, however, be detected in some cases. The contribution of these background contaminants to concentrations in a 1000-L water sample was a maximum of 1 pg/L for an individual organochlorine compound or 1 ng/L for an individual nonchlorinated hydrocarbon. We assume, therefore, that the values reported for chlorinated organics are not too high because of contamination during sampling or analysis. Other peaks appearing in the chromatograms of blanks, primarily early eluting, low molecular weight compounds, were not identified and did not interfere with the compounds reported. Because the levels of many compounds in seawater are extremely low, and since the introduction of contaminants into the procedures is probably nonrandom and of variable magnitude, the determination of background values with appropriate confidence intervals has posed a major problem. However, increasing the volume of seawater sampled (the supplies of which are not limited) reduces background contamination to a small portion of measured levels.

The concentration of PCBs determined with the system described range from less than 1 pg/L in the Eastern Pacific (Table 5) to 660 pg/L in San Francisco Bay (Table 3), with intermediate values in coastal waters near San Francisco (Table 2) and in the Southern California Bight (Table 4). Toxaphene levels in the Eastern Pacific (Table 5; Fig. 5, bottom) were 52 ± 5 pg/L (SD, identification confirmed by GC/MS). The reported concentrations of *p,p'*-DDE, *p,p'*-DDD, total alkanes, and total UCM of the saturated fraction have not been corrected for background contamination.

Two PPF columns were mounted in series during

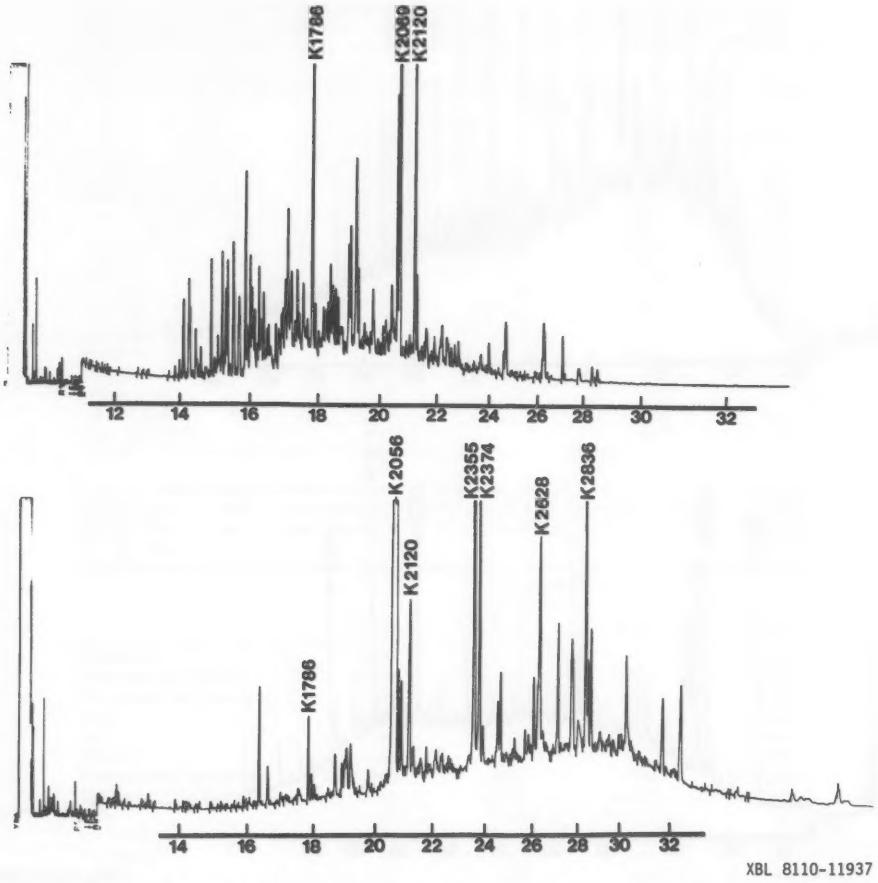

FIG. 4. FID chromatograms of aromatic fractions of dissolved and particulate phases of seawater sampled in the vicinity of Angel Island, San Francisco Bay, August 3–4, 1980. Kovats 1786, phenanthrene; Kovats 2069, fluoranthene; Kovats 2120, pyrene; Kovats 2056, heneicosahexaene.

collections in San Francisco Bay and the Southern California Bight. The analyses of these columns (Tables 3, 4) showed that the second column contained only about 1% of the *p,p'*-DDE measured in the first column. Since each column was subjected to identical and simultaneous procedures during preparation, sampling, and laboratory analysis, the *p,p'*-DDE concentration reported in the second column might be taken as the maximum level of the background in this system. Similarly, the values reported from the second column for other compounds measured (Tables 3–5) also provide maximum background concentrations. Many of these values are in the 1 pg/L range, significantly below those of the first column.

RECOVERY FROM THE PARTICULATE PHASE

The recovery of most nonchlorinated hydrocarbons associated with the particulate phase appeared to be quantitative, since the composition and concentrations of hydrocarbons retained on the filters were invariably distinct from those recovered from the dissolved phase. In the sample from San Francisco Bay (Table 3; Fig. 3), the saturated fraction of the dissolved phase contained a mixture of lower molecular weight alkanes in the ratios characteristic of crude oil. The resolved components in the particulate phase, however, were principally biogenic compounds. The relatively high levels of alkanes n-C_{27}, n-C_{29}, and n-C_{31} indicate a contribution from terrestrial plants (Simoneit 1977, 1978, 1980). The cluster of peaks in the vicinity of Kovats' index 2100 may represent phytadienes, which like alkanes n-C_{15} and n-C_{17} are biogenic hydrocarbons synthesized by marine algae (Lytle et al. 1979).

In the aromatic fraction, the compounds retained on the filter were not detected in the dissolved phase or were

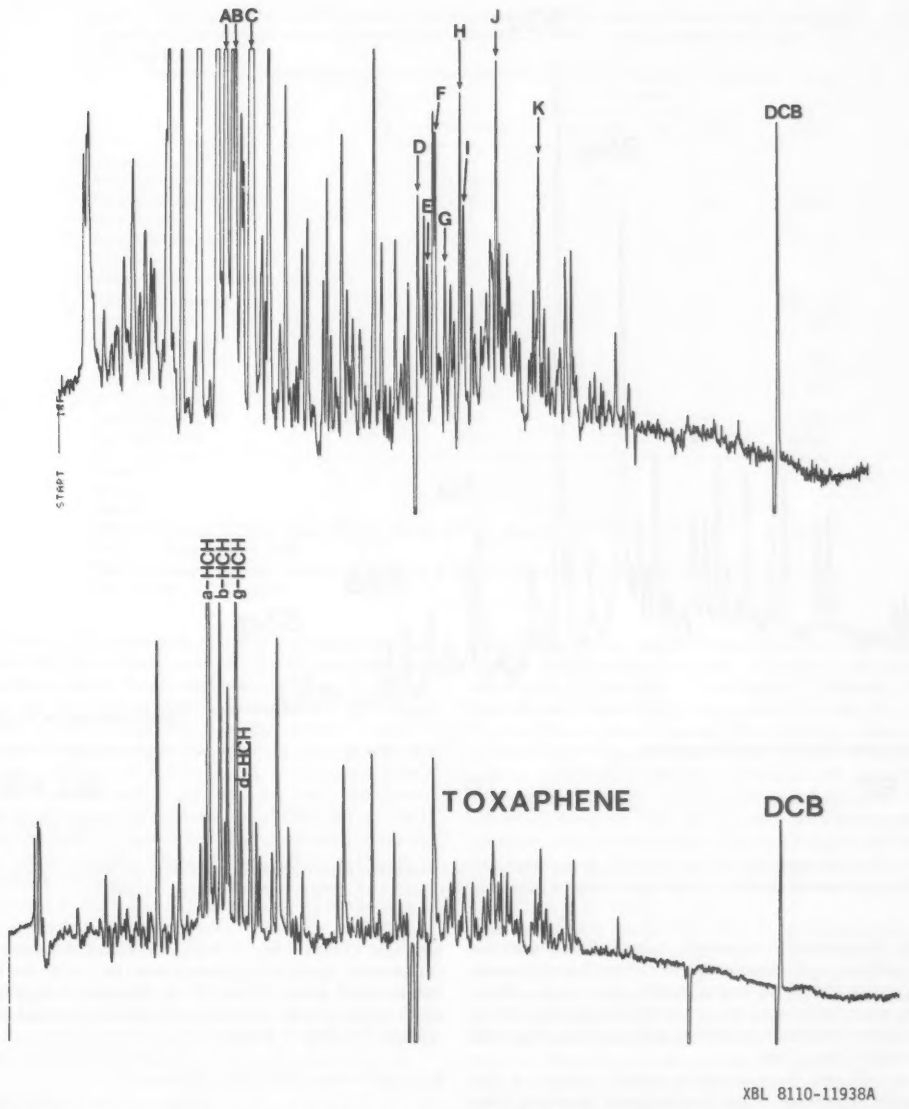

FIG. 5. Electron capture chromatograms of the aromatic fraction extracts of the dissolved phase of seawater from the Southern California Bight in the vicinity of Santa Barbara Island, October 16–17, 1980 (top) and the eastern Pacific Ocean (bottom) (see Table 5); 30-m fused silica SE-30 capillary column. A, α-HCH; B, β-HCH; C, γ-HCH; D, γ-chlordane; E, *o,p'*-DDE; F, α-chlordane; G, *trans*-nonachlor; H, *p,p'*-DDE; I, *o,p'*-DDD; J, *p,p'*-DDD; K, *p,p'*-DDT, coeluting with another compound; DCB, decachlorobiphenyl, internal standard.

present in comparatively low amounts (Fig. 4). The compound with Kovats' index 2056 is the hexaolefin *cis*-heneicosa-3,6,9,12,15,18-hexaene, a component of many species of marine algae (Blumer et al. 1970). MS analysis showed that compounds with Kovats' indexes 2355, 2374, 2628, and 2836 (squalene) were also biological compounds but that other resolved components in the particulate phase were polynuclear aromatics in the same relative proportions as those produced by pyrogenic activity (Hites et al. 1977; Lee et al. 1977; Laflamme and Hites 1978; Windsor and Hites

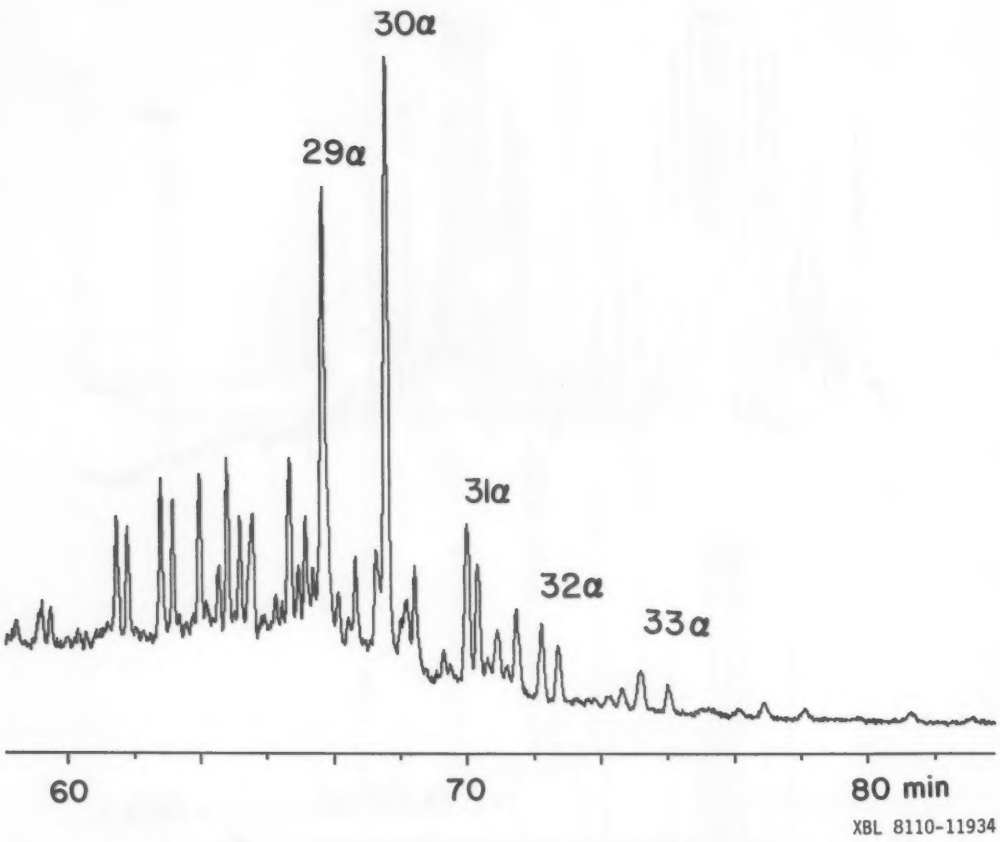

FIG. 6. Ion chromatogram, M/z 191, showing a profile of pentacyclic triterpanes in ratios characteristic of a crude oil. Extract of the saturated fraction of the particulate phase of seawater sampled at Angel Island, August 3–4, 1980 (compare with Fig. 3, bottom).

1979). Phenanthrene was present in both phases, with the concentrations in the dissolved phase (1.9 ng/L) being somewhat higher than those in the particles (1.3 ng/L). Partitioning observed between the dissolved and particulate phases is in agreement with the solubilities of the various compounds in seawater (May 1980).

Data obtained from the other samples examined also showed a separation in the distribution of individual compounds between the particulate and dissolved phases (Tables 2–5). Among the chlorinated compounds, PCBs and *p,p'*-DDE were distributed in both phases in approximately equivalent amounts (Tables 2–4), although the majority of the *p,p'*-DDT was in the particulate phase (Tables 3 and 4). In all areas sampled, the hexachlorocyclohexane (HCH) compounds were predominantly in the dissolved phase (Tables 2–5) (confirmed by GC/MS in the sample from the eastern Pacific). The majority of the chlordane compounds were in the dissolved phase in water of the Southern California Bight (Table 4; Fig. 5, top), but in San Francisco Bay the particles contained approximately the same levels as the dissolved phase (Tables 2, 3). Dieldrin, endosulfan I, and toxaphene were predominately in the dissolved phase (Tables 3, 5; Fig. 5, bottom).

RECOVERY FROM THE DISSOLVED PHASE

Recovery from the dissolved phase by the PPF column was examined by the separate analysis of extracts from two columns mounted in series and by intercalibration with liquid–liquid extraction using cyclohexane as the extracting solvent (Tables 1–5). Values obtained by the foam and liquid–liquid systems for aromatic hydrocarbons, PCBs, and α-chlordane were equivalent (Table 2). High retention efficiency of polynuclear aromatic compounds by PPF has been demonstrated by Basu and Saxena (1978a, 1978b). The levels of PCBs, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, α- and

TABLE 6. Concentration of total hydrocarbons and estimates of total petroleum within the boiling range of n-C_{14} and n-C_{35} in seawater of the California coast and offshore, 1980 (nanograms per litre, corrected for recovery (see text)).

Site	Saturates		Aromatics		Total
	Resolved	Unresolved	Resolved	Unresolved	
San Francisco Bay[a]					
Total hydrocarbons	170	1700	140	200	2200
Total petroleum	15	1700	12	200	1900
Eastern Pacific[b]					
Total hydrocarbons	13	<15	57	<13	70–98
Total petroleum	<1	<15	<1	<13	<30
Southern California Bight[c]					
Total hydrocarbons	75	<30	40	<12	120–160
Total petroleum	<5	<40	<5	<15	<65
Coastal Los Angeles[d]					
Total hydrocarbons	41	260	42	97	440
Total petroleum	25	260	15	97	400
San Diego Harbor[e]					
Total hydrocarbons	1000	2700	160	1500	5400
Total petroleum	1000	2700	35	1500	5200

[a]Table 3.
[b]Table 5.
[c]Table 4.
[d]Moving transect between Santa Monica Beach to Point Fermin (34°0.05'N, 118°33.5'W to 33°40.5'N, 118°18'W), October 8–9, 1980.
[e]Moving transect between nautical buoy No. 8 at harbor entrance and nautical buoy No. 32 in the upper harbor, October 13–14, 1980.

γ-chlordane, *trans*-nonachlor, toxaphene, phenanthrene, and pyrene in the first columns were an order of magnitude more concentrated than in the second columns (Tables 3–5), indicating that the conditions employed allowed quantitative recovery of these compounds from the dissolved phase. A similar two-column sampler has been used to determine the collection efficiency of PPF in extracting chlorinated hydrocarbons from air (Burdick and Bidleman 1981). Because of the efficient retention by the foam of *p,p'*-DDE and *p,p'*-DDT the higher values reported for these compounds from the liquid–liquid assembly (Table 2) are probably the result of background contamination.

Recovery of the γ-HCH compounds by PPF was significantly lower than that of the liquid–liquid system (Table 2). The poor retention of the HCH compounds by PPF columns was also indicated by the relatively high amounts, between 15 and 60% of the amounts in the first columns, found in the second column of two mounted in series (Tables 3–5). Similarly, recovery from the dissolved phase of the lower boiling alkanes by a single column was relatively low (Table 3).

MEASUREMENTS OF PETROLEUM

Previous studies have used the presence of an unresolved complex mixture (UCM) and a homologous series *n*-alkanes with an odd to even ratio near unity as an indication of petroleum contamination (Boehm 1980; Burns and Smith 1980; Matsumoto and Hanya 1981). In this study, the unresolved mixture of the saturated fraction of the particles from San Francisco Bay (Fig. 3) was shown to contain petroleum compounds using MS analysis. An ion chromatogram for M/z 191, a characteristic ion of the pentacyclic triterpanes, is shown in Fig. 6. The pattern of these compounds, all with the 17-α(H) configuration, indicates a geochemically mature source such as petroleum (Dastillung and Albrecht 1976; Simoneit and Kaplan 1980). The extended hopanes (C_{31}, C_{32}, C_{33}) (Fig. 6) are present as pairs of enantiomers with a concentration ratio of approximately unity, a result of thermally induced racemization during maturation and genesis of petroleum (Crisp et al. 1979; Dastillung and Albrecht 1976; Simoneit and Kaplan 1980). Detection of these compounds in extracts of seawater and marine organisms has provided definitive evidence of the presence of petroleum and clues as to its origin (Simoneit and Kaplan 1980; Anderlini et al. 1981; Risebrough et al. 1983).

At the eastern Pacific site (Fig. 2), petroleum mixtures could not be detected in either the dissolved or particulate phases (Fig. 6; Table 6). The biological compounds detected are common to many samples of California marine waters (B. W. de Lappe and R. W. Risebrough, unpublished data). The total unresolved components are present at concentrations less than 20 ng/L, a level near the sampling and analytical background. Similarly, petroleum could not be detected (<65 ng/L total petroleum) in the waters of the Southern California Bight which receive petroleum compounds from a number of natural seeps (Simoneit and Kaplan 1980), shipping, and coastal discharges. Input into the Bight of hydrocarbons in surface runoff from the Los Angeles River has been estimated to be in the order of 10^4 t/yr (Eganhouse and Kaplan 1981). Only at sites immediately offshore and in harbors and bays could petroleum be detected by the sampling and analytical methodologies employed (Table 6). In estimating the contribution of saturated hydrocarbons in the levels of total petroleum, corrections for recovery were made

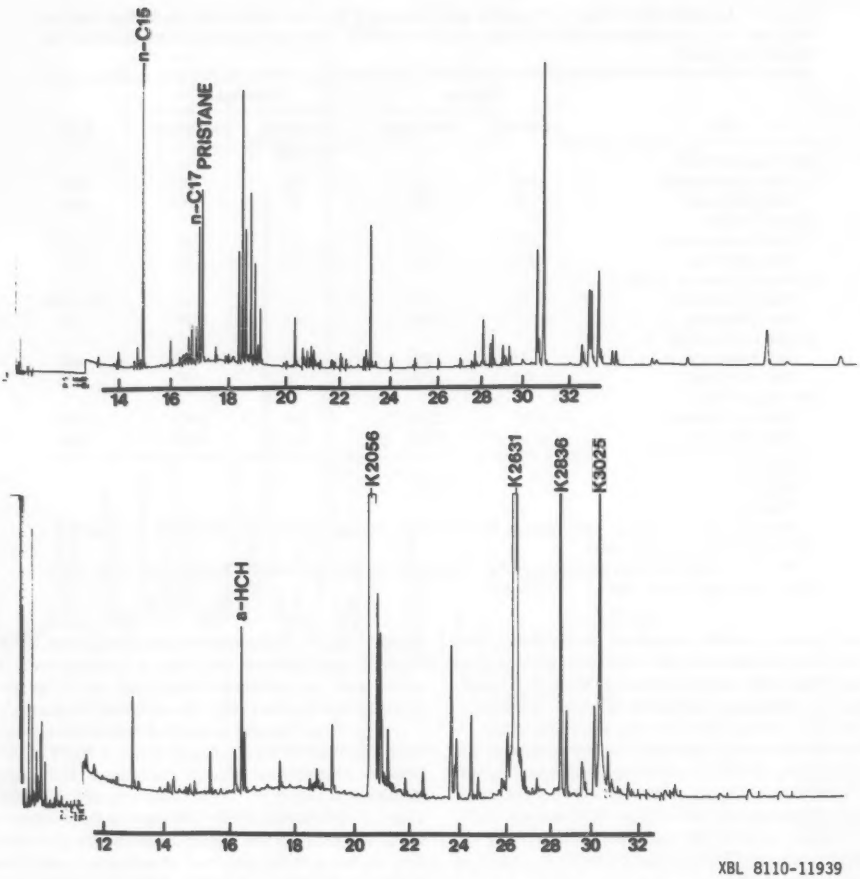

FIG. 7. FID chromatograms of the saturated (top) and aromatic (bottom) fractions of the particles in seawater sampled during a transect between 35°55′N, 123°35′W and 35°38′N, 123°34′W, September 28–29, 1980 (4261 L).

with the equation

$$(1) \quad c = \frac{ab}{b-1}$$

where c is the true concentration in the dissolved phase, a is the estimated concentration based on retention by the first column, and b is the ratio of the amount of the compound in the first column to the amount in the second (see below).

Ultraviolet fluorescence spectroscopy, which measures the aromatic component of extracts, has been widely used in estimating the concentrations of petroleum in seawater (Brown and Searl 1976; Brown and Huffman 1976, 1979; Gupta et al. 1980; Gupta and Kureishy 1981; Keizer et al. 1977; Law 1978, 1981; Levy 1979). With this method, however, estimates for total petroleum are frequently higher than the maximum concentration recorded in the present study (5 μg/L) in San Diego Harbor (Table 6). Since a high recovery of aromatic compounds is attained using PPF column extraction (Table 3), there is an apparent discrepancy in the values provided by the two methodologies. An intercalibration of these two techniques, with concurrent field sampling, should be undertaken.

SAMPLER DESIGNS: SOME CONSIDERATIONS

With liquid–liquid extraction systems it is not practical to obtain samples of volumes greater than 100 L; both solvent volume and flow rate are limiting. Detection limits for this technique are usually in the microgram per litre range (Otson and Williams 1981). The difficulties of working with liquid–liquid systems under shipboard conditions, including the problem of obtaining backgrounds lower than the environ-

mental concentrations of several of the compounds and compound classes measured, make the use of solid adsorbents for seawater sampling desirable.

In the present study, a sample volume of 2000 L permitted the GC/MS confirmation of the identification of toxaphene in the dissolved phase of seawater present at concentrations in the order of 50 pg/L. A sample volume of 4261 L at the same site in the eastern Pacific permitted the conclusion that concentrations of total petroleum in the combined particulate (Fig. 7) and dissolved phases were less than 30 pg/L (Table 6). Sample volumes in the order of 100 L would not have provided material sufficient for similar detailed chemical analyses. Clearly, larger sample volumes increase both the analytical and interpretative capability; as discussed above, they also serve to reduce the relative magnitude of the background contamination.

Simon and Bidleman (1979) and Burdick and Bidleman (1981) examined an air sampling system for the movements of individual chlorinated biphenyl compounds using a column of 15 foam plugs, 7.6 cm diameter × 1 cm thick, under experimental conditions in the laboratory. After a single application, individual compounds were found to move through the column as if it were a chromatographic system, with the order of elution paralleling that from a GC column. The penetration of an isomer band maximum was linearly related to total air volume. When the chlorinated compounds were continuously bled from a coated glass bead reservoir into the airstream, each compound moved through the column in a broad front, with progressive saturation of successive plugs. There was, however, significant forward tailing, with a proportionate reduction in the amounts of a given compound in successive plugs. Our estimates of the total petroleum component of the saturated hydrocarbons in waters sampled assume that comparable forward tailing existed in the two-column system, and equation 1 was applied. Confirmation of this assumption, and satisfactory determinations for compounds such as the HCH group, would require increasing the number of independent adsorptive units in series to permit better estimates of recovery and determination of background values for the compounds detected. The foam system described could also be improved by increasing the diameter of the adsorptive units, permitting an increase in flow rate.

The sampling system described is adequate for the determination of a number of synthetic organic compounds, intermediate molecular weight aromatic hydrocarbons, and many biogenic compounds in subsurface seawater. Measurements of their concentrations would be useful in the formulation of global mass balance equations for the synthetic organics and for petroleum, in studies of global transport, and in studies of biological processes in the sea.

Acknowledgments

Research was supported by the Bodega Bay Institute, by the Mussel Watch Program of the U.S. Environmental Protection Agency, and by the Division of Ocean Sciences, National Science Foundation (OCE80-01727). Mass spectrometric analyses were performed using facilities of the Lawrence Berkeley Laboratory, which we thank for cooperative support. We thank William R. Sistek and David R. de Lappe for their assistance in sampling and sample preparation.

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Fate and Transport of Selected Herbicides in an Estuarine Environment[1]

J. C. MEANS

Chesapeake Biological Laboratory and Department of Chemistry, University of Maryland, Solomons, MD 20688-0038, USA

AND R. D. WIJAYARATNE AND W. R. BOYNTON

Chesapeake Biological Laboratory, University of Maryland, Solomons, MD 20688-0038, USA

MEANS, J. C., R. D. WIJAYARATNE, AND W. R. BOYNTON. 1983. Fate and transport of selected herbicides in an estuarine environment. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 337–345.

Representative compounds from three classes of herbicides (atrazine, linuron, and treflan) were studied to determine ambient levels in the Chesapeake Bay and its tributaries during portions of 1980. All levels were 1 μg/L or less, and all three herbicides exhibited non-conservative behavior in the estuary. Concentrations of herbicides in runoff from a defined watershed did not exceed 9 μg/L. Degradation rates for all three herbicides in estuarine sediment–water systems were 2–10 times greater than those reported for soils. Equilibrium sorption constants (K_{oc}) of estuarine sediments were similar to soils, but suspended colloids were found to sorb atrazine and linuron 10–30 times more strongly on a per gram of carbon basis, suggesting that refractory hydrophobic pollutants may be transported greater distances in the water column than previously assumed. However, the large degradative capacity of the estuarine community may act to prevent transport of labile organics from the land to the oceans.

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Des composés représentatifs de trois classes d'herbicides (atrazine, linuron et tréflan) ont été étudiés afin d'en mesurer les niveaux ambiants dans la baie de Chesapeake et ses tributaires à certaines époques de 1980. Les niveaux sont de 1 μg/L ou moins, et les trois herbicides ne sont pas persistants dans l'estuaire. Les concentrations d'herbicide dans l'écoulement d'un bassin hydrographique défini ne dépasse pas 9 μg/L. Les taux de dégradation des trois herbicides dans des systèmes sédiments estuariens–eau sont de 2 à 10 fois supérieurs à ceux qui ont été mentionnés pour les sols. Les constantes de sorption d'équilibre (K_{oc}) des sédiments estuariens sont identiques à celles des sols, mais on constate que les colloïdes en suspension sorbent l'atrazine et le linuron à des concentrations de 10 à 30 fois plus fortes, sur base de carbone par gramme, ce qui donne à penser que les polluants hydrophobiques réfractaires peuvent être transportés à de plus grandes distances dans la colonne d'eau qu'on ne le croyait. Cependant, il est possible que la grande capacité de dégradation de la communauté estuarienne empêche le transport des composés organiques labiles depuis la terre jusque dans les océans.

Received March 19, 1982
Accepted November 25, 1982

Reçu le 19 mars 1982
Accepté le 25 novembre 1982

THE increasing use of pesticides for weed and insect control in the modern agricultural practices of North America has been a major factor in expanding production. Annual application of herbicides in the United States currently exceeds 300 000 t of active ingredients (Berry 1979). Of the more than 140 herbicidal agents in use, the *s*-triazines constitute approximately one-third of all herbicides used, with the compound atrazine constituting approximately 80% of total *s*-triazines. Two other major herbicidal classes used widely on the Eastern seaboard of the United States and Canada are the phenylureas (primarily linuron) and trifluralin (treflan).

Herbicides that are applied in agricultural regions of the Eastern coastal plains of Canada and the United States may enter the oceans by way of a number of estuaries, the largest of which is Chesapeake Bay. Concern has developed in recent years because of the potential environmental damage to estuarine and coastal marine ecosystems which are dependent on

[1]Contribution No. 1140 of the Center for Environmental and Estuarine Studies, University of Maryland. This work forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J6873)
Imprimé au Canada (J6873)

the photosynthetic capacity of primary producers (Wu et al. 1980). In Chesapeake Bay, the precipitous decline (>90%) of several species of rooted aquatic macrophytes has lead to an intensive study of the effects of agricultural runoff upon rooted aquatic plant communities (Stevenson et al. 1982). The present study is one component of that research effort and focuses upon chemical and physical factors which influence the transport of herbicides in estuarine systems.

The transport of herbicides into aquatic systems is a function of the runoff from the watershed, the persistence of the compound in soil, the water solubility of the herbicide, the degradation rate of the compound, and the sorption of the compound on soils, sediments, and suspended particles. A large number of estimates of amounts of herbicides in runoff have been made. The estimated percentage of applied herbicide leaving the field in runoff for the three compounds investigated in this study are as follows:

	Range (% of applied)	Mean (% of applied)	Reference
Atrazine	0.02–17.0	2.86	Schueler 1979
Linuron	—	0.30	Willis et al. 1975
Treflan	0.03–0.17	0.10	Willis et al. 1975

These values, combined with the recommended application rates for active ingredients (2, 1.5, and 0.8 kg/ha for atrazine, linuron, and treflan, respectively), allow estimation of loading rates if the watershed area is known.

The persistence of the herbicide in surficial soils varies with application rate, soil type, moisture, pH, and organic matter and clay content (Wauchope 1978). Stewart et al. (1975) estimated the persistence of atrazine, linuron, and treflan in Chesapeake Bay regional soil types at 12.5, 4.2, and 5.0 mo, respectively. Although estimates vary, the typical water solubilities cited for atrazine, linuron, and treflan are 33, 75, and 0.05 mg/L, respectively (Wauchope 1978).

The affinity of herbicides for soils, suspended particles, and sediments will influence the fate of herbicides in aquatic systems. The sorption properties of atrazine, linuron, and treflan have been studied extensively on a wide variety of soils. The adsorption constants, K_{oc}, have recently been reviewed by Rao et al. (1982). One important substrate property that appears to control the strength of sorption of hydrophobic herbicides is soil organic matter (Bailey and White 1970). Therefore, the individual sorption constants (K_d) are often normalized for the weight fraction of organic carbon of the substrate to yield the constant K_{oc} which is unique for the compound sorbed. The typical values of K_{oc} for atrazine, linuron, and treflan are 170, 860, and 670, respectively (Rao et al. 1982; Farmer 1976). The value of K_{oc} for a given compound is highly correlated with the water solubility (Chiou et al. 1979; Means et al. 1980) and with the octanol–water partitioning coefficient, K_{ow} (Karickhoff et al. 1979; Means et al. 1979; Means et al. 1980), of the compound. No studies of the sorption of these herbicides on estuarine sediments appear in the literature.

In this study, we present data on (1) the distribution of selected herbicides in both water and sediments in the Chesapeake estuary during the 1980 growing season, (2) adsorption coefficients for the three herbicides on representative estuarine sediments, and (3) adsorption coefficients of atrazine and linuron on estuarine colloidal matter. Data on the degradation rates of these herbicides in estuarine sediment–water systems as compared with soil systems are also presented and discussed. Finally, the implications of the above information and results for the fate of herbicides in estuarine environments are summarized.

Materials and Methods

Twenty-eight sampling stations were selected for study in littoral zones (approximately 1 m in depth) of the upper and middle regions of Chesapeake Bay as well as two tributaries (Fig. 1). The stations were selected to be representative of (1) the spatial distribution of submerged macrophytic vegetation in Maryland waters of Chesapeake Bay, (2) land use patterns (e.g. farms, forest, marsh, residential, etc.), and (3) estuarine morphology (e.g. coves, open shore, tributary). Each station was sampled for herbicide residues in water and sediment during the months of April, June, July, and September of 1980. Sediment samples for sorption studies were collected in September 1980 at three stations (Fig. 1). These stations were selected to encompass characteristic sediment types present in Chesapeake Bay as determined from Maryland State Geological Survey sediment maps. The estuarine colloidal samples used in this study were collected on the Patuxent and Choptank rivers at the stations designated in Fig. 2.

Collection of Samples

Two-litre samples of water were collected at mid-depth (0.5 m below the surface) at each station in new glass jars that were precleaned with distilled water, chloroform, acetone, and pesticide-grade methanol. The sample container was rinsed with sample water twice before filling. The jars were then capped with precleaned Teflon-lined caps and stored at 4°C in the dark until analyzed. Maximum storage time was 5 d until extraction. Stability studies were conducted to insure that no degradation occurred during this storage period.

Sediment samples for residue analysis were collected at each station using a stainless steel cylindrical coring probe. The cores were extruded onto solvent-cleaned aluminum foil, and the top 5 cm of each core was then transferred to a precleaned glass sample jar with a Teflon-lined cap. Typically, three to five such cores were taken at each site and combined. Sediment samples were frozen at −40°C until analyzed.

Sediments for sorption studies were collected using a van Veen grab. These sediments were wet sieved through a 2-mm-mesh screen and air-dried. Samples were stored at 25°C in glass containers until used.

Estuarine colloidal material was obtained by collecting 20 L of estuarine water at 0.5 m below the surface. An enriched colloidal fraction (ECF) of about 350 mL was obtained using Amicon H_1P_5 hollow fiber filtration apparatus (Means and Wijayaratne 1982). If stored, the ECF was preserved with 1 mL of 1.0 g sodium azide/L and refrigerated at 4°C in the dark. A portion (5–7 L) of each ultrafiltrate (UF)

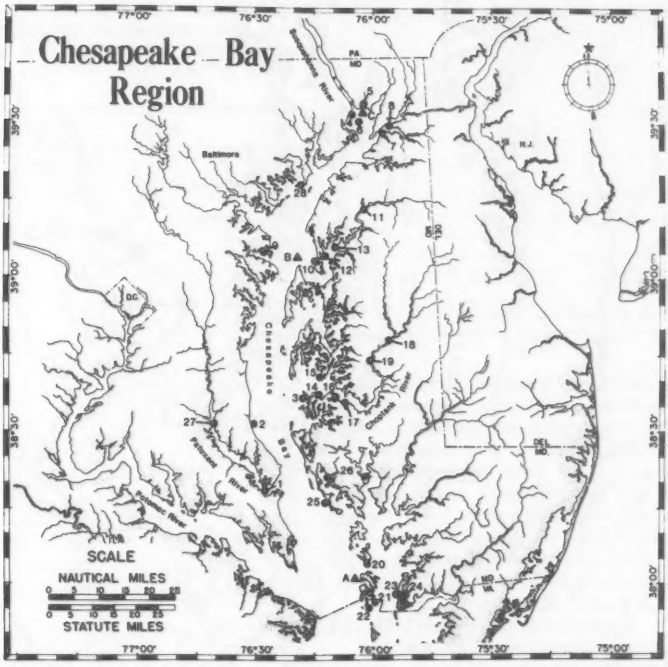

FIG. 1. Locations of water and sediment (●) sampling stations on Chesapeake Bay and sediments for sorption studies (▲).

was retained and preserved in the same way to serve as a diluent for the ECF. The organic carbon contents of the ECF and UF were determined on an Oceanography International dissolved carbon analyzer using the persulfate oxidation method.

HERBICIDE RESIDUE DETERMINATIONS

The concentrations of atrazine, linuron, and treflan in water samples, sediments and colloids were determined by high-performance liquid chromatography (HPLC) using a modification of the method of Means et al. (1982). One-litre samples of 0.45-μm Millipore filtered water were passed through a Sep-pak C_{18} cartridge at a rate of 3 mL/min and desalted with 10 mL of deionized water. The cartridges were eluted with 10 mL of pesticide-grade methanol. The methanol was then evaporated under nitrogen, and the residue was taken up in a known volume of acetonitrile for analysis.

Wet sediment samples (equivalent to approximately 50 g, dry wt) were extracted in a Soxhlet apparatus for 24 h using pesticide-grade acetonitrile. The extracts were dried over anhydrous Na_2SO_4 and evaporated in two steps using a rotary vacuum evaporator followed by a stream of nitrogen. The extract was dissolved in a known volume of acetonitrile for analysis.

The detection limit of the method described for the three herbicides is 0.05 μg/L for water samples and 0.10 μg/kg for sediments, with a precision of ± 0.005 μg/L.

SORPTION EQUILIBRIA ON SEDIMENT AND ESTUARINE COLLOIDS

Sorption equilibria were determined for atrazine, linuron, and treflan on three Chesapeake Bay sediments. The specific protocols are outlined in detail in Means et al. (1979). In all cases, the equilibrium solution concentrations were selected to be 10% or less of the water solubility of the compound to avoid saturating the solid phase.

Equilibrium isotherms were also determined for atrazine and linuron on partially enriched solutions of estuarine colloidal material. Aliquots of ECF (50−70 mL) were added to 1 L of UF containing a known quantity of atrazine or linuron. The spiked samples were equilibrated in a constant-temperature shaker for 18 h at 20°C and then recirculated through the hollow fiber system to separate the ECF and UF (dissolved) portions. The hollow fibers were rinsed with 20 mL of distilled water to insure complete removal of the enriched colloidal matter. The herbicide contained in each fraction was determined by HPLC, as described early in Materials and Methods. The amount of herbicide sorbed to the colloid was then calculated by difference.

In all cases, experiments were performed to ensure that no

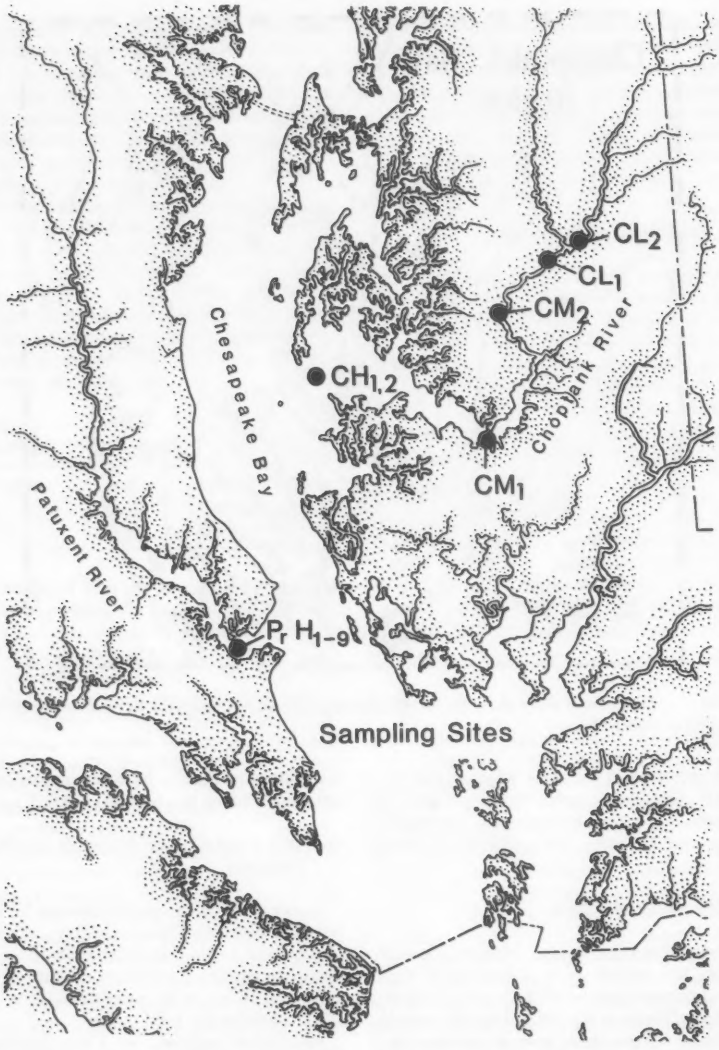

FIG. 2. Location of colloid sampling stations on the Choptank and Patuxent rivers in Chesapeake Bay.

degradation occurred during the course of the study, and a mass balance was determined in the colloid sorption studies.

GEL PERMEATION STUDIES

The molecular masses of estuarine colloidal fractions and the retention characteristics of herbicides and herbicide–colloid complexes were determined by gel permeation on Sephadex G-25. A bed of G-25 gel preswelled with water was prepared in an all glass–Teflon column (2.9 cm inside diameter × 15 cm). Samples of ECF or herbicide solutions (500 μL) were injected into the column which was maintained at a flow rate of 1.3 mL/min. The column effluent was monitored with an ultraviolet detector (254 nm). The exclusion and inclusion volumes were determined by using a blue dextran standard and NaCl solution, respectively. The column was calibrated for molecular mass using a standard series of proteins (Waters Associates).

TABLE 1. Maximum herbicide concentrations (micrograms per litre) observed at 28 stations on the Chesapeake Bay during April, June, July, and September 1980. The month during which the maximum occurred is in parentheses. ND = less than detection limit = 0.05 mg/L.

Station	Atrazine	Linuron	Treflan
1	0.97 (Sept.)	ND	ND
2	0.80 (June)	0.31 (Sept. + July)	ND
3	ND	ND	ND
4	1.1 (June)	ND	ND
5	0.2 (Apr.)	0.8 (July)	ND
6	1.2 (June)	ND	ND
7	1.05 (June)	ND	ND
8	0.7 (June)	1.3 (July)	ND
9	ND	0.56 (July)	ND
10	ND	ND	ND
11	ND	ND	ND
12	ND	ND	ND
13	0.11 (Sept.)	ND	ND
14	ND	ND	ND
15	0.1 (Apr.)	ND	ND
16	ND	ND	ND
17	0.2 (Apr.)*	ND	ND
18	0.1 (Apr.)	ND	ND
19	0.1 (June + July)	ND	ND
20	ND	ND	ND
21	0.1 (June)	ND	ND
22	0.2 (July)	ND	ND
23	ND	ND	ND
24	0.3 (Apr.)	ND	ND
25	0.1 (Apr.)	0.05 (July)	ND
26	ND	ND	ND
27	0.99 (Sept.)	0.76 (Apr.)	ND
28	0.09 (June)	ND	ND

*Only sampled in April.

Results and Discussion

DISTRIBUTION OF HERBICIDES IN CHESAPEAKE BAY

Throughout the year, the levels of atrazine and linuron observed in the water column were low (1.3 μg/L or less) (Table 1). In general, the highest concentrations were observed early in the growing season (April or June), just after herbicide application (April) and after the first major runoff event of the year (June). Peak concentrations of linuron were observed at only a few stations and tended to occur later in the growing season. This is in part due to the fact that linuron is generally used as a postemergent herbicide, while atrazine is applied as a preemergent and often preplant treatment. Detectable levels of treflan were not found at any of the stations during the months that they were sampled.

The spatial distribution of the peak concentrations of the herbicides atrazine and linuron indicated that (1) the highest concentrations of atrazine were always observed at the head of Chesapeake Bay near the mouth of the Susquehanna River, suggesting that this very large tributary supplying over 70% of the freshwater input might also be the major source of this herbicide in the Bay, (2) other secondary concentration maxima, where observed, tended to be isolated and therefore associated with localized diffuse sources, and (3) the herbicides were not distributed conservatively over the salinity range sampled either in the bay mainstem or within the tributaries of the Choptank and Patuxent rivers. These data are consistent with those of J. Austin (USEPA, Annapolis, MD, personal communication) and J. Ward (U.S. Geological Survey, Reston Center, Reston, VA, personal communication) who periodically monitored levels of atrazine and simazine levels in water of the Susquehanna River and the upper third of Chesapeake Bay during the years of 1977, 1978, and 1979. They are also consistent with the results of Hershner et al. (1981) who monitored levels of atrazine in Virginian areas of Chesapeake Bay.

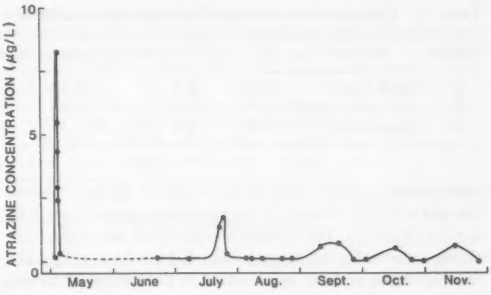

FIG. 3. Herbicide runoff concentration during five runoff events during May–November 1980.

Sediment analyses indicate that no detectable residue concentrations (>0.10 μg/kg) of any of the three herbicides were present in any of the surficial sediments during the 1980 growing season. These data are consistent with those of Hershner et al. (1981) who sampled and analyzed a comparable number of sediment samples for atrazine in the lower third of Chesapeake Bay and several tributaries.

The nonconservative distribution of herbicides in the bay could be the result of one or more factors including degradation, sorption, volatilization, or small low-level pulses of herbicide input followed by rapid dilution to undetectable levels. To examine the latter phenomenon at a more controllable level we monitored atrazine runoff concentrations from a defined watershed on University of Maryland property. The concentrations of atrazine (the only herbicide applied in the watershed) in runoff during the period from early May through the end of 1980 are shown in Fig. 3. The May samples represent the first major runoff event following herbicide application in late April 1980 at a rate of 2.0 kg/ha. It is clear that the major pulse of herbicide transported to the estuary coincided with the first runoff event following application. Herbicide runoff during later runoff events was significantly decreased until an apparent steady state was achieved in the latter months of the year. Therefore, the timing of water sampling relative to the most recent runoff event may account in part for the "patchiness" of bay herbicide levels.

SORPTION STUDIES ON CHESAPEAKE BAY SEDIMENTS

The adsorption properties of Chesapeake Bay sediments are an important factor in determining the distribution and fate of

TABLE 2. Characteristics of selected Chesapeake Bay sediments.

Station	Sediment	pH	Salinity (‰)	% organic carbon
A	Smith Island	5.05	20.9	0.93
B	Chester R. mouth	6.53	12.5	2.66
C	Furnace Bay	5.71	0.2	2.54

hydrophobic organics such as herbicides in the bay system. The pH's of 1:1 slurries of the sediments ranged from 5.05 to 6.53 (Table 2). The salinity regimes from which the sediments were collected ranged from 0.2 to 20.9 g/kg. The organic carbon content, as measured by the method of Allison (1965), ranged from 0.93 to 2.66% by weight, indicating that these sediments fall within the range used to characterize the sorption properties of hydrophobic compounds in previous studies (Means et al. 1980).

Equilibrium sorption isotherms determined for all three herbicides on three sediments were linear over the range of solution concentrations (Fig. 4). The K_d values or Fruendlich distribution coefficients for atrazine, linuron, and treflan ranged from 1.98 to 3.19, 9.26 to 20.0, and 6.05 to 14.6, respectively (Table 3). When the K_d values were normalized for the organic carbon content of the sediments, the resultant K_{oc} values tended to converge on 139 ± 68 for atrazine, 833 ± 145 for linuron, and 576 ± 74 for treflan. These values compare quite well with the average K_{oc} values for soil cited earlier (170, 860, and 670, respectively). These data suggest that a range of typical Chesapeake Bay sediments are capable of sorbing hydrophobic herbicides and that the strength of sorption is comparable with that observed in a wide variety of soils.

SORPTION PROPERTIES OF ESTUARINE COLLOIDAL MATTER

The absence of detectable residues of several classes of herbicides in bay sediments with typical sorption properties in the presence of detectable levels of the same herbicides in the overlying water suggests that some other processes are active in the estuary which alter the sediment–water partitioning equilibrium. Hassett and Anderson (1979) suggested that colloidal matter in freshwater systems might be capable of binding hydrophobic organic molecules.

Data for estuarine colloidal matter indicate that this material has a strong sorption capacity for hydrophobic organic molecules (Means and Wijayaratne 1982). The equilibrium adsorption isotherms for atrazine and linuron on ECF (enrichment factor = 2 in isotherm mixtures) from natural water ultrafiltrates were linear over the range of equilibrium solution concentrations tested, suggesting that the amount of herbicides adsorbed in these experiments was within the sorptive capacity of the colloids. The amount of sorbed herbicide was normalized on a per gram of carbon basis because (1) the amount of carbon associated with the colloid was the most precise measure available for monitoring the amount of colloid present in both the bulk water and in the colloid-enriched water and (2) organic matter is the portion of many environmental substrates (i.e. sediments, soils, microorganisms, etc.) that controls the adsorptive behavior of many nonpolar organic compounds (Karickhoff et al. 1979; Means et al. 1980).

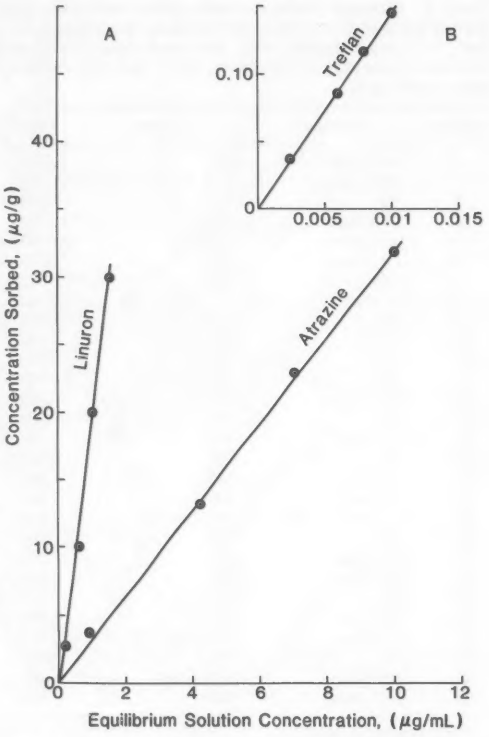

FIG. 4. Equilibrium adsorption isotherms (at 25°C) for (A) atrazine and linuron and (B) treflan on Furnace Bay sediment.

The slopes of the isotherms determined by linear regression correspond to the K_{oc} derived from the Fruendlich equation (Table 4). The K_{oc} values for atrazine on colloids collected from low-, medium-, and high-salinity regions of the Choptank River during September 1980 were 8540, 7930, and 4840, respectively. In all cases, the coefficients of determination (r^2) were 0.992 or greater.

Another set of colloid samples collected in February 1981 was used to develop isotherms for both atrazine and linuron. Linear isotherms were obtained for both compounds on the colloids; however, the slopes obtained for atrazine were lower than those observed for colloids from a comparable salinity regime (Table 4). The ratio of atrazine to linuron K_{oc} values was, however, similar to that observed in sediment–soil systems (170 vs 670 for soil as compared with 1850 vs 6750 for colloid).

The high K_{oc} values for colloidal matter suggest that atrazine and linuron are strongly bound. On an organic carbon basis, the colloidal material is 10–35 times better as a sorptive substrate for the herbicides than sediment or soil organic matter, although there are large differences in colloids collected in different subestuarine rivers during different times of

TABLE 3. Sorption coefficients of atrazine, linuron, and treflan on selected Chesapeake Bay sediments.

Station	Sediment	% organic carbon	Atrazine			Linuron			Treflan		
			K_d	r^2	K_{oc}	K_d	r^2	K_{oc}	K_d	r^2	K_{oc}
A	Smith Island	0.93	1.98	0.993	213	9.26	0.999	996	6.05	0.999	651
B	Chester R. mouth	2.66	2.08	0.999	78	19.1	0.999	717	13.4	0.995	503
C	Furnace Bay	2.54	3.19	0.999	126	20.0	0.985	787	14.6	0.993	575

TABLE 4. Chemical characteristics and sorption constants for atrazine and linuron on estuarine colloids.

Sample code[a]	Date	Salinity (g/kg)	Total organic carbon (mg/L)			Herbicide	K_{oc}[b]
			Initial bulk water	Final UF	ECF		
CL_1	Aug. 1980	1.24	3.63	2.01	98.6	Atrazine	13 600
CM_1	Aug. 1980	9.92	3.34	1.56	108.5	Atrazine	4 860
CH_1	Aug. 1980	14.2	3.25	1.51	104.6	Atrazine	6 990
CL_2	Sept. 1980	1.50	3.85	2.35	65.5	Atrazine	8 540
CM_2	Sept. 1980	5.71	3.40	2.11	74.2	Atrazine	7 930
CH_2	Sept. 1980	17.0	3.24	1.56	59.3	Atrazine	4 840
P_rH_1	Feb. 1981	19.1	2.93	2.06	33.5	Atrazine	1 690
P_rH_2	Feb. 1981	11.0	2.93	2.01	33.5	Atrazine	2 141
P_rH_3	Feb. 1981	14.6	3.23	2.01	44.0	Atrazine	1 850
P_rH_4	Feb. 1981	13.5	3.26	1.83	49.0	Linuron	6 760
P_rH_5	Feb. 1981	14.5	3.31	1.76	52.5	Linuron	6 210
P_rH_6	May 1981	14.9	3.23	2.01	43.0	Atrazine	1 850
P_rH_7	May 1981	11.9	3.23	2.01	43.0	Atrazine	1 790
P_rH_8	May 1981	11.9	3.23	2.01	43.0	Linuron	6 810
P_rH_9	May 1981	11.9	3.23	2.01	43.0	Linuron	6 420

[a]C = Choptank River samples, P_r = Patuxent River samples, L, M, H = low, medium, high salinity, respectively.
[b]Correlation coefficient (r^2) = >0.992.

the year. There are two hypotheses that may explain the difference between K_{oc}'s observed on soils−sediment and on colloidal matter. First, although K_{oc} values are reported on a total organic carbon basis for a soil or sediment, all of the organic carbon is not available as a sorptive surface. Soil−sediment organic matter is itself sorbed to a highly porous and irregular matrix, often occupying or filling in micropores in the structure. If it is assumed that the soil−sediment organic matter is not a monomolecular film, then K_{oc} values calculated on a total carbon basis may be low by 1−2 orders of magnitude. This would shift the average K_{oc} for atrazine to values in a range comparable with that observed in the present experiments. Alternatively, the surface acidity of sediment or soil clay particles may have the effect of decreasing the sorptive capacity of the organic matter (Means and Wijayaratne 1982).

The effects of such variables as pH and salinity on sorption of herbicide to estuarine ECF have been reported in an earlier paper (Means and Wijayaratne 1982). Additional variation observed in the sorption of atrazine, on colloids in particular, collected at different times and places in the estuary may be due to differences in the composition of the colloids. Estuarine colloidal matter consists of proteinaceous−carbohydrate polymers which are associated with varying amounts of poorly crystallized clay minerals (Sigleo and Helz 1981; Sigleo et al. 1982; Wijayaratne 1982). These authors report that while the colloid is substantially carbonaceous (>90% organic) in the spring and summer months, the relative proportions of inorganic matter increase in the winter (>20−30%, inorganic). Typical elemental compositions of the organic fraction are 35−45% carbon, 35−45% oxygen, 4−6% hydrogen, and 4−6% nitrogen. If, as we have hypothesized above, inorganic matter is decreasing the sorptive capacity of the organic fraction present, then this could account for the decrease in K_{oc} observed for atrazine on colloids collected in February 1981 as compared with those collected in August and September 1980.

GEL PERMEATION STUDIES

Gel permeation techniques were used to verify that the herbicides were sorbing to the colloids and to estimate the molecular mass range of colloids involved in the sorption process. The nominal molecular mass of the estuarine colloids was 12 000 daltons. When either atrazine or linuron solutions were passed through the column, they eluted at the inclusion volume of the column, as verified by the coelution of NaCl. However, when equilibrated colloid and herbicide solutions were injected, the herbicides coeluted with the 12 000-dalton portion, well before the NaCl eluted.

TABLE 5. Degradation rates of selected herbicides in soils and sediments.

System	Herbicide	Half-life (days)	Reference
Soil	Atrazine	64	Armstrong et al. 1967
Soil	Atrazine	110	Jones et al. 1982
Soil	Atrazine	36	Jones et al. 1982
Soil	Atrazine	64	Dao et al. 1979
Lake sediment	Atrazine	145	Armstrong et al. 1967
Estuarine sediment (8‰)[a]	Atrazine	16	Jones et al. 1982
Estuarine sediment (15‰)[a]	Atrazine	13	Jones et al. 1982
Soil	Linuron	78	Moyer et al. 1972
Soil	Linuron	87	Hance 1974
Soil	Linuron	58	Urosol and Hance 1974
Soil	Linuron	180	Urosol and Hance 1974
Estuarine sediment (18‰)[a]	Linuron	6	Means et al. 1983
Estuarine sediment (12‰)[a]	Linuron	12	Cunningham et al. 1981
Soil	Treflan	154	Kearney et al. 1976
Soil	Treflan	93	Parr and Smith 1973
Soil	Treflan	85	Probst et al. 1967
Soil	Treflan	54	Zimdahl and Gwynn 1977
Estuarine sediment (18‰)[a]	Treflan	9	Means et al. 1983

[a]Studies performed in conjunction with the present study at the University of Maryland.

DEGRADATION OF HERBICIDE IN ESTUARINE SEDIMENT–WATER SYSTEMS

To more fully address the issue of herbicide dynamics in the Chesapeake Bay, we embarked upon an extensive study of the degradation of three herbicides in estuarine sediment–water systems using outdoor test microcosms. The scope of these experiments is too large to report as part of this paper; however, the results are summarized in Table 5 and the implications complement other aspects of this paper. Some of the available rates of herbicide degradation in soil systems (Table 5) are contrasted to half-lives determined for estuarine systems in our studies. For all three herbicides it is clear that the degradation rates in estuarine sediments were significantly more rapid than in soils. Half-lives in estuarine systems were from 2 to 10 times shorter for atrazine, 8–30 times shorter for linuron, and 5–15 times shorter for treflan than in soils. These data are consistent with and partially explain the observation that herbicide residues are not observed at detectable levels in Chesapeake Bay sediments. It appears that the increased diversity of organisms in estuarine sediments are capable of degrading herbicides which sorb to the sediments at rates which preclude accumulation of analytically detectable residues.

General Discussion

Data for three herbicides indicate that concentrations in estuarine waters were generally low to undetectable during the 1980 growing season and were distributed nonconservatively in the estuary. Although estuarine sediment sorbed herbicides with K_{oc}'s comparable with those of soils, detectable residues of the herbicides were not accumulating in Chesapeake Bay sediments. The (K_{oc}'s) of estuarine colloidal matter were from 10 to 30 times greater than those observed for sediment–soils on a per gram of carbon basis. Thus, it appears that natural colloids may be important in the transport of hydrophobic contaminants in the aquatic environment. Partitioning of solutes onto these colloids is highly dependent upon bulk water characteristics such as pH and salinity and upon colloid composition (e.g. organic to inorganic ratio, molecular mass, etc.). The high K_{oc} values for colloid–herbicide sorption may be reflected by higher herbicide levels in estuarine water relative to sediments, and may enhance such degradation processes as photolysis. Herbicide degradation rates were from 2 to 30 times faster in estuarine sediments than in soils.

In summary, although Chesapeake Bay receives a significant loading of herbicides from the Susquehanna River and its other tributaries, these materials do not appear to be transported out of the estuary to the ocean, nor are they accumulating in Bay sediments. Degradation studies suggest that the microflora and fauna of Bay sediments can degrade these and potentially other contaminants at greatly accelerated rates relative to soil environments. This estuary, as well as others, appears to have the potential to serve as a buffer between contaminated coastal rivers and the oceans. However, the high sorptive capacity of estuarine colloidal organic matter relative to sediments may provide a mechanism by which more refractory organic compounds such as chlorinated hydrocarbons can be mobilized from estuaries into the oceans at rates more rapid than previously anticipated.

Acknowledgments

We thank the following people for their assistance in the field and the laboratory: N. Kaumeyer, A. Pait, C. Hetfield, and M. Meteyer. This research was supported by USEPA grants R805932 and X003 248010 from the Chesapeake Bay Program.

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Session IV — Summary and Overview: Organic Synthetics

JOHN W. FARRINGTON

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

AND JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

Research concerned with pollutant organic compounds in the marine environment, particularly surface and deep waters well away from coastal areas, has been severely restrained by controversies about contamination problems and artifacts introduced during the sampling and analysis procedures. de Lappe et al. report on the progress by their group in solving this vexing problem. They report that a system using polyurethane foam as a solid absorbant, mounted in line with a glass fiber filter, has the required capability to isolate several organic pollutants from seawater in amounts sufficiently above blanks to allow for measurements of 1×10^{-12} g/L organochlorine pesticides in particulate and dissolved phases with samples of over 1000 L. Capabilities were also convincingly demonstrated for measuring individual fossil fuel compounds when total petroleum was present at 100×10^{-12} g/L. Although the present system only samples surface waters, packaging with appropriate power sources, pressure casings, and electronics appears to be tractable and will allow applications to deeper water measurements.

As Professor Goldberg has set forth in his stimulating paper, there are many concerns, particularly in the Southern Hemisphere, about the extent of organochlorine contamination in the oceans. We cannot accurately describe global or regional biogeochemical cycles for these compounds in seawater unless we have more and better oceanic water column measurements. de Lappe et al. contributed a significant start towards this goal by designing, constructing, and evaluating the performance of their system and applying it to the measurement of organochlorines and several fossil fuel compounds at eight California coastal locations and a station in the eastern Pacific 200 km off the California coast.

Mackay and co-workers present a lucid summary of the physical–chemical concepts applied to model air–sea exchange of organic contaminants. Such theoretical frameworks are needed as a critical part of the environmental scientific research triumvirate of theoretical calculations, experimentation, and field observations. Mackay et al. also conducted laboratory experiments in 6-L systems to investigate conformance to theoretical prediction for exchange of hydrocarbons from water to the atmosphere with and without particulate matter present. The results generally agreed with the theoretical prediction, except that the critical parameters of oil droplet size and particulate matter size are difficult to estimate or measure with required accuracy and precision. Thus, reasonable theoretical calculations cannot be made to check against experimental results.

The half-lives for several compounds, such as the volatile liquid hydrocarbons benzene, toluene, xylenes, *n*-octane, and *n*-decane, were on the order of 30–150 min for volatilization from solution, and with half-lives extending to 200 min for oil dispersion conditions.

These results from Mackay et al. provide an interesting contrast to the field observations of Wakeham et al. from Narragansett Bay, Rhode Island, and were the subject of lively discussion. The latter authors used sophisticated high-resolution glass capillary gas chromatography (GCGC) and GCGC–mass spectrometry to measure a wide range of volatile organic compounds along a transect in Narragansett Bay during two summer and two winter seasons. Their results clearly indicated that municipal and industrial waste waters at the head of the bay were major sources of chlorinated C_2-hydrocarbons (e.g. tetracholorethylene), chlorobenzenes, and aromatic hydrocarbons). Concentrations of chlorinated hydrocarbons and fossil fuel hydrocarbons decreased in the transect from the head of the bay towards the midbay area. Volatilization exchange to the atmosphere appeared

Printed in Canada (J7254)
Imprimé au Canada (J7254)

to be a major removal process for these compounds in both winter and summer. However, the calculated half-lives are on the order of 100−200 h in both summer and winter in comparison with 30−150 min in the laboratory experiments of Mackay et al.

Various explanations may account for this discrepancy. It is difficult to mimic the complexities of an aquatic ecosystem in a laboratory flask. It is equally as difficult to maintain control of or make enough measurements to constrain actual ecosystem complexities for the purposes of unequivocal modeling. The value of both approaches is clearly demonstrated in this case. Both groups of workers are forced to a healthy reexamination of their data and interpretations. Are turbulence conditions and surface film thicknesses adequately simulated or accounted for in both instances? What are the roles of various physical and chemical forms in governing the rates of loss to the atmosphere? The results of Mackay et al. suggest that there is a reduction in the rate of loss for a portion of the volatiles in their dispersion experiment.

Despite the disagreement as to the actual rate of loss, it is comforting that *both* experiments and field observations agree that volatilization is a major process controlling loss of volatiles from the upper portions of the water column. The data and interpretations of Wakeham et al. also show that biological degradation of aromatic hydrocarbons is an important removal process in the summer and that sorption of volatiles onto suspended particulate matter and subsequent sedimentation may be important only for aliphatic hydrocarbons within the classes of volatile compounds considered in these studies.

The research of Means and co-workers demonstrated the importance of sorption for higher molecular weight compounds of environmental concern. Their field observations in Chesapeake Bay and selected tributary rivers and laboratory experiments concerned with the herbicides atrazine, linuron, and treflan made significant contributions to our understanding the environmental behavior of these compounds in estuarine and coastal ecosystems. Low concentrations of herbicides of 1 μg/L or less were found in the estuary and they exhibited nonconservative mixing behavior. Equilibrium sorption constants related to organic carbon content in sediment (K_{oc}) were similar to K_{oc} values of soil for these herbicides.

A most important contribution by Means et al. was the formulation and experimental verification of the concept that colloidal organic matter in aquatic systems can have a significant influence on the biogeochemistry of the herbicides and, by logical extension, of other hydrophobic pollutants and naturally occurring organic compounds. The K_{oc} values demonstrated that colloids sorbed 10−30 times more linuron and atrazene than an equivalent weight of sediment. The physical dynamics of colloids, e.g. resuspension and transport, in estuarine and coastal systems are obviously going to be different than for particulate matter.

Better predictive capabilities and understanding of the biogeochemistry of synthetic organic pollutants in estuarine, coastal, and open ocean ecosystems were achieved by de Kock through his field observations of PCBs in *Mytilus edulis* transplanted to Dutch coastal waters. In this extensive application of the transplanted sentinel organism concept, de Kock has convincingly demonstrated the biological availability of significant amounts of PCBs to Dutch coastal areas from the Rhine−Meuse and Scheldt systems. The concentration of PCBs in the mussel tissue at the site of the natural population was in the range of 0.09×10^{-6} to 0.86×10^{-6} g/g ash-free dry weight of tissue. After transplanting to various stations in Dutch coastal waters, the concentrations increased to 2×10^{-6} to 16×10^{-6} g/g ash-free dry weight of tissue. Other workers have documented the extent of PCB input to the area by rivers and the accumulation of PCBs in sediments. However, the relationship between the total PCB geochemical cycle in this area and the biogeochemical cycle of biologically available PCBs is not yet well known, as pointed out by de Kock.

It seems reasonable to predict that application of the sampling and analytical methodology of the type reported by de Lappe et al., coupled with the transect type studies of Wakeham et al., and further research into the importance of colloidal, solution, and particulate matter interactions will be among the key efforts of the future in connecting the

geochemical cycle of total PCBs with the biogeochemical cycle of biologically available PCBs and, by analogy, other similar compounds.

Another interesting feature of the paper by de Kock is the comparison of the Dutch coastal data for PCBs with data for Cd and the differences in the biogeochemistries of these two types of chemicals after both are delivered by river input to the estuarine–coastal areas. The comparison of the Dutch coastal data for Cd and PCBs in mussels is compared with data from the United States coast and the other European coastal areas. The sentinel organism approach to coastal and estuarine chemical pollutant monitoring using cosmopolitan species such as mussels and oysters has and is producing sets of data that allow reasonable comparisons between areas of the world; these comparisons should be useful to evaluation and promulgation of regulations, to remedial actions, and to guiding research.

Can the Oceans Be Protected?[1]

EDWARD D. GOLDBERG

Scripps Institution of Oceanography, La Jolla, CA 92093, USA

GOLDBERG, E. D. 1983. Can the oceans be protected? Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 349–353.

Effective regulation of marine pollutants is now hampered by problems associated with the magnitude of man's activities. Increasing numbers and quantities of contaminants lead to increasing uncertainties about sources and inputs, more interaction between pollutants and between pollutants and organisms, and increasing difficulties in elucidating the dynamics of contaminants. The examples of global toxaphene contamination, coastal eutrophication, and continuing use of chlorinated hydrocarbons are used to illustrate an optimistic prognosis and a need for increased levels of funding for ocean studies, long-term studies of ecological processes of unperturbed systems, greater involvement of international agencies, and refinement of remote sensing techniques.

GOLDBERG, E. D. 1983. Can the oceans be protected? Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 349–353.

Les problèmes associés aux activités humaines de grande envergure empêchent actuellement le contrôle efficace des polluants marins. Des nombres et des quantités toujours croissantes de contaminants rendent de plus en plus incertains les sources et les apports, accentuent l'interaction entre polluants et entre polluants et organismes, et, enfin, compliquent de plus en plus l'élucidation de la dynamique des contaminants. Nous donnons des exemples de contamination globale par le toxaphène, d'eutrophisation côtière et d'usage continu d'hydrocarbures chlorés pour illustrer des prévisions optimistes et la nécessité de crédits accrus pour financer des études océaniques, des études à long terme des processus écologiques de systèmes non perturbés, une plus grande participation des organismes internationaux et le raffinement de techniques de télédétection.

Received October 15, 1982
Accepted February 25, 1983

Reçu le 15 octobre 1982
Accepté le 25 février 1983

IT is inevitable that the marine environment will change continuously in the future. An increasing world population will be using greater and greater amounts of materials. Modern society is a disposing, not an accumulating, entity. Materials will pass through it in general only once. Disposal of societal waste will take place in the oceans, on land, and in the atmosphere. Most of the material is benign and will neither interfere with life processes nor damage the environment. However, a part of the waste is dangerous and can jeopardize the resources of our surroundings. Herein, I will consider present abilities to predict which materials, either deliberately or inadvertently introduced to the oceans, can have an unacceptable impact on its resources and to evaluate the findings through field programs. Such predictions are crucial to decision making as to whether to produce a hazardous material at all, or, if produced, where and how to safely dispose of it.

The Stepping Stones to Controlling Marine Pollutants

The first recognition that the composition of the oceans can be adversely affected by industrial societies came about in the early 1950's with the development of nuclear energy. Scientists in the United States, United Kingdom, and the USSR were well aware that the promiscuous release of radioactive waste products to the marine environment could adversely affect public health through consumption of contaminated food or through exposure at soiled coastal zones. Acceptable levels of artificial radionuclides in the environment were then computed on the basis of protecting critical populations with the highest potential exposures. Monitoring programs were initiated to ensure compliance by dischargers for permissable releases. For example, the effective management of direct entries of radioactive wastes from the British Windscale facilities, where the reprocessing of nuclear fuels takes place, to the Irish Sea have been carried out over the past decades without any apparent effect on public health of the British population (e.g. Pentreath 1982). Similar husbandry of radioactive wastes has been accomplished by many countries

[1]This paper forms part of the Proceedings of the Conference on Pollution in the North Atlantic Ocean, convened at Halifax, Nova Scotia, October 19–23, 1981.

Printed in Canada (J7089)
Imprimé au Canada (J7089)

including France, India, USSR, and the United States. It is important to realize that the awareness of dangers and the steps to reduce them were developed by scientists in these countries and presented to receptive political entities responsible for the management of marine resources.

During the last few decades, several tragedies alerted the scientific and political communities to serious marine pollution problems. The Minimata Bay episode in Japan directed attention to the careless discharge of waste chemicals from a plastic manufacturing plant with a consequential epidemic of methyl mercury poisoning (Officer and Ryther 1981). Mercury was used as a catalyst in the production of the plastics. The mercury compounds entered the fish and shell fish eaten by the Minimata Bay residents. Scholarly inquiry into the toxicology and environmental behavior of mercury followed along with monitoring programs to ascertain if there were any other undesirable releases of this element to the coastal ocean.

Another tragedy involved the biocide DDT whose extensive agricultural and public health usages brought its dispersion about the environment to over 100 000 t/yr in the late 1960's. Although the chemical was initially effective against some of the pests it was intended to control, nontarget organisms were also disastrously decimated. With time, some target organisms developed resistances to it (W.H.O. 1979). In the early 1970's the general use of DDT and other chlorinated hydrocarbon pesticides was restricted by the United States and many northern European countries. Of importance is the criterion for the outlawing of its use: unacceptable effects on nontarget organisms and the loss of the integrity of ecosystems both on land and in the sea.

These three examples, artificial radionuclides, DDT, and mercury contamination of the marine environment, have several common threads that have transformed environmental problems into success stories. First, the cause–effect relationships between the chemical culprit and the victim could be established. In the cases of mercury and DDT, the body burdens of the affected species could be related to the biological effects and to the environmental levels. In the cases of the radioactive substances, there were substantial biological data with which to predict unacceptable body burdens based on known effects of ionizing radiation.

Second, an active scientific corps and environmental groups existed who were able to bring about a translation of conventional wisdom into public policy. The numbers of involved persons were small, be they scientists, environmentalists, or public servants. The combination of these circumstances led to effective regulation of identifiable chemicals that could endanger the quality of life in the industrialized world.

The Tyranny of Size

As we enter the 1980's it appears to me that the problems of protecting the oceans from man's discards are becoming formidable. This is a consequence of what might be called "the tyranny of size." With increasing industrialization there are larger numbers of polluting chemicals entering the oceans that increase the burden of contaminants. These chemicals may act in concert or antagonistically on the ocean's flora and fauna. Although we have more scientists with more elegant and sophisticated equipment, the data that they produce is poorly managed, especially with regard to its use in predicting problems. Further, a large part of it is irrelevant. Much of the marine environmental investigations appears to follow Hare's Law: you never do anything for the first time or for the last time. As a consequence, urgently needed studies are overlooked, while routine and often useless information is churned out. There has evolved a herd of environmental administrators some of whom have built up bureaucratic infrastructures that interfere with the effective prosecution of scientific inquiry.

Many of the scientific problems, although perhaps tractable, are requiring greater and greater efforts. For example, there are still to be developed field techniques to measure the biological impact of pollutants. It is often difficult to distinguish between natural and man-induced effects, whether they be behavioral, biochemical, physiological, or ecological.

Also, the inputs of polluting materials on national or global bases are often poorly known. Often, production and use data and the amounts and composition of discharged wastes are proprietary information of economic value to industries or countries. However, the problem of obtaining such data in a form or in a way that does not jeopardize the producer has been solved in some instances (i.e. the fluorocarbon production on a world-wide basis). Yet, general protocols to obtain the numbers are yet to be formulated. Although registries of toxic chemicals have been proposed in some international agencies, these remain to be established.

Three problems will be examined to elaborate upon the difficulties in evaluating the present and future health of the ocean: difficulties related to the "tyranny of size." The possibility of a global pollution problem involving "toxaphene" disturbs many environmental scientists, as does the apparent increasing trend toward eutrophication of coastal marine waters. The continued use of chlorinated hydrocarbons as pesticides, especially in developing countries, provides a third example. Other groups of pollutants could equally well have been used as case examples including the chlorination and ozonation products from water treatment plants, which are long-lived and apparently building up in nearshore waters, and the petroleum hydrocarbons. A more complete list of marine pollutants of general concern is itemized in NOAA (1979).

The Toxaphene Problem

The argument that toxaphene may be a serious concern has been raised in several places. Holden (1981) poses the problem quite directly: "Toxaphene has been given as an example of an organochlorine which may be widely distributed in the European environment but is still not generally recognized even fifteen years after Jensen identified PCB's. . . In a recent analytical intercalibration exercise for organochlorines conducted by ICES, three of the more advanced laboratories which participated reported substantial concentrations of toxaphene in the distributed sample. . . . Most analysts taking part in the exercise did not mention toxaphene, but some said they could not detect it, although it seems likely that a relatively high concentration was present in the sample. . . . The reported concentrations. . . exceeded the total of all other organochlorines found. . . toxaphene should now be included

in routine analyses for organochlorine residues in the European marine environment, and the analytical techniques must be adjusted to enable the residues to be isolated."

Soren Jensen, in an invited lecture on toxic substances at the fifth International Symposium on Environmental Geochemistry (Stockholm, June 1–5, 1981), posed the same concern. Toxaphene may be a global pollutant whose environmental concentrations may be building up to levels that threaten the health of living organisms.

Toxaphene is a set of chloroorganic compounds resulting from the photochlorination of the oil of turpentine. There are over 175 distinguishable compounds, the so-called polychlorocamphenes, but only a few have been uniquely identified. On the other hand, there are two principal isomers of DDT. Thus, the analysis of toxaphene, through gas chromatography, is about 100 times less sensitive than that of DDT. Toxaphene is most difficult to assay in environmental samples.

Unlike DDT and its degradation products, toxaphene shows little or no photoreactivity. Its environmental residence times thus may be higher than those of DDT and its residues, which are photoreactive, if nonbiological processes are in part regulatory.

Toxaphene has been produced since the late 1940's and its production rate in the United States in recent times is approximately 2.2×10^{10} g/yr (1975). World production figures in the 1970's appear to be about 5×10^{10} g/yr, of the same order of magnitude as the peak values for DDT.

Although organochlorine insecticides have been used less and less in recent years in the Northern Hemisphere, toxaphene still is in widespread use, especially in cotton agriculture (NAS 1981). During the period 1964–76 the use of toxaphene has doubled in the United States and has become the single most used pesticide on a weight basis, with the organophosphate, methylparathion, following closely behind. Usage of toxaphene in 1976 was approximately 11800 t (26 million pounds) for cotton protection. In the United States it is registered for use on many vegetable, fruit, and grain and fodder crops as well as directly on livestock.

Unlike DDT, toxaphene is mutagenic in the *Salmonella* test (Hooper et al. 1979). Clearly, all of its components may not be mutagenic. But workers assessing the risk involved with the continued introduction of toxaphene to the environment cannot overlook this observation.

There are few dedicated analyses of toxaphene in the literature. Zell and Ballschmiter (1980) suggested that the polychlorocamphenes may have been mistaken for PCB's. These workers indicate that "the production figures for toxaphene, its tendency for bioaccumulation and its persistence in the environment. . . (make) a world wide occurence of (it) by no means surprising."

Is toxaphene an environmental problem or not? The answer remains to be found, yet we have an American scientific community that has not given this set of compounds a systematic evaluation as an environmental pollutant.

Can We Carry Out a Surveillance Program for Toxaphene?

Can we develop a strategy to determine the levels of toxaphene in the coastal waters of the United States? Most probably. The Mussel Watch Program, sponsored by the Environmental Research Laboratory of the Environmental Protection Agency, carried out a monitoring program during 1976–78 at somewhat over 100 stations around the east, west, and gulf coasts. Four groups of pollutants were analyzed in the soft tissues of mussels and bivalves: heavy metals, artificial radionuclides, petroleum hydrocarbons, and halogenated hydrocarbons (Goldberg et al. 1978). Coastal zones that carried unusually high burden of pollutants in their waters were singled out. For example, high levels of DDT were found in mussels in the area of a sewer outfall near Los Angeles where wastes from its manufacture were discharged. Unacceptable levels of PCB's were found in commercially caught fish from New Bedford Bay, Massachusetts, after the mussels in the waters were shown to have markedly higher concentrations of PCB's than those in adjacent unpolluted waters.

As a part of the Mussel Watch Program, the subsamples from the 100 stations annually visited were frozen for future use. Thus, there are available for the years 1976, 1977, and 1978 potentially recoverable records of toxaphene in the bivalves that can be compared with those in presently living mussels. Increases or decreases in the toxaphene levels over the period 1976–81 can then be ascertained.

A new sampling year is possible. The strategies for collecting the samples under uniform conditions and for sending them rapidly in a frozen state by air to the analytical facilities are well developed. There are at least a half dozen laboratories in the United States capable of carrying out the toxaphene analyses. What is initially lacking is the funding for the program. But there are other problems that work against an effective activity.

The husbandry of the data that would be generated for appropriate assessment should be carried out with modern computer facilities. Yet such are as yet not available to the marine pollution scientific community. The amount of data that might be generated by such a program is large. Let us assume that 400 samples for 1976, 1977, 1978, and 1981 are assayed for 10 components, whose capillary column gas chromatographic characteristics are identifiable at the participating laboratories. Thus, there will be over 4000 numbers to be dealt with on time and space bases.

The Trend Toward Coastal Water Eutrophication

The toxaphene problem is probably one of short term. The effectiveness and hence use of this biocide will probably decrease with time as the target organisms develop resistances to it. Thus, it will probably enter the ocean for a few decades at most, although the problems that can potentially be created by its presence may be of longer duration. Perhaps one of the more serious problems on a long-term basis for the coastal ocean and estuaries is the general trend toward eutrophication as a consequence of the introduction of increasing amounts of phosphate and nitrate by industrial, social (detergents), and agricultural activities. It appears that on a global basis over the last 30 yr, nitrate has increased 15-fold and phosphate has increased 5-fold in the rivers entering the oceans. Further, with increased discharges to the coastal waters of industrial and domestic wastes and with deforestation and land use

changes, there has been a significant entry of anthropogenic organic carbon.

As a consequence, there has been an increase in phytoplankton production and alteration of their species composition (NOAA 1979). The diatoms, which are the food base for filter-feeding fishes and zooplankton and which support largely the coastal commercial fishery, are being displaced by the dinoflagellates. These latter organisms are a poor food substitute for the diatoms. Further alterations of the community structure can also occur. The biostimulants can enhance the production and range of macrophytes (sea grasses and attached algae).

However, there are other effects of the increasing flux of nutrients and organic matter to the marine environment. Because of the increased productivity, there is an increased flux of organic matter to the sediments. Anoxic conditions are developing over larger areas and there may be changes occurring in the structure of the benthos. There may be an increased entry of carbon dioxide into the waters in these areas as a consequence of increased respirational activity. This may result in a dissolution of calcium carbonate in the sediments, an effect that has not, as yet, been observed.

The trend towards anoxia may be self-sustaining. The increased flux of organic matter into the sediments may be compensated by an increase flux of nutrients out of the sediments. Following oxidation of the organic matter in the sediments, the nitrate and phosphate ions can return to the water column. Coupling this flux with that of the rivers and coastal runoff to the surface waters can result in further enhanced productivity, and the formation of organic matter can become self-sustaining.

Biomass increases, anoxia, and alteration of the community structure has been observed worldwide in coastal waters and in estuaries (NOAA 1979). Chesapeake Bay, the New York Bight, the southern and northern California coasts, the Baltic Sea, Kaneohe Bay, Hawaii, the Adriatic Sea, Oslo Fjord, Omura Bay (Japan), and Tokyo Bay (Japan) are but a few of the zones subjected and responding to these anthropogenic stresses of increased inputs of biostimulants. Still, our observational and predictive activities have not been terribly intensive, although many consider this problem to have a very high priority in our goals of protecting the oceans. What types of information are needed to assess the seriousness of the problem?

Perhaps one of the most important needs is an ability to distinguish between natural and man-induced phenomena in the coastal area and the magnitudes of each. This is a most difficult task. Needed are long-term ecological studies of the natural variations in populations of marine ecosystems, unaffected by human activity. Such projects in selected coastal areas might require time periods of decades and should include intertidal muddy ecosystems, intertidal rocky coasts, mud bottom communities, sand bottom communities, and pelagic planktonic communities in bays or estuaries.

Other Pesticides and the Literature Watch

I suspect that the literature on marine pollution, grey and otherwise, doubles in a time period of less than a decade, if it follows the multiplication factors of other areas of environmental sciences. How well is this literature watched by national and international bodies for descriptions of present oceanic problems and for predictions of future ones? There are abstracting services, such as Marine Pollution Abstracts and Deep-Sea Research Abstracts, that provide the background information for assessments for the health of oceanic areas. But is this literature systematically combed for those substantial researchers that give guidance to those who are protecting the marine environment? I believe the answer is no.

Every so often I come across an investigation that suggests a problem is in need of detailed further evaluation and perhaps extended field and laboratory studies, e.g. remarkably high concentrations of total DDT and of HCH (1,2,3,4,5,6-hexachlorocyclohexane including the α, β, η, and δ isomers) in the air off the western coast of India, total DDT in the air in the Pacific off Central America, and high HCH in the air off southern Asia (Tanabe and Tatsukawa 1981). These HCH measurements are the first extensive results published for the open-ocean environment. The authors suggest that the cumulative world production of HCH is over 1×10^6 t, perhaps approaching that of DDT. Large amounts of HCH are consumed, for example, in India as a biocide. The higher water solubility and high vapor pressures of HCH species, compared with those of DDT, suggest that a substantial sink may be found in the surface waters of the ocean.

Tanabe and Tatsukawa (1981) indicated that there are most probably extensive uses of both pesticides in developing countries, especially those in tropical zones. Their distributions in midlatitude airs of the Pacific simply cannot be explained by Japan as the only source. Japan banned the use of both pesticides several years before the measurements were made and the concentration in the coastal marine environment reflected this action. On the other hand, the open-ocean waters surrounding Japan showed uniformly high values after the ban.

Tanabe and Tatsukawa (1981) suggested that atmospheric transport is moving these pesticides from their sources about the tropical and midlatitudes. They are concerned about an undesirable impact on the marine environment. I agree that the problem they state is worthy of attention. But who is joining them in a greater effort to understand the source terms and the potential effect upon life in the sea? Who is willing to serve as a protector of the oceans?

Can We Protect the Oceans?

I submit that the answer is yes. Although the problems are much more formidable than in the past several decades, there is much evidence that their solutions will be found. First, the priority concerns are being enunciated. The necessary information to pose options for their resolution is being sought by a few, but dedicated, innovative investigators. A corps of competent scientists able to cope with the demands of regulatory groups is being trained and the efforts of United Nations agencies along these lines in the developing world appear successful. Intergovernmental groups, such as ICES and GIPME, are carrying out the housekeeping chores: arranging for interlaboratory comparisons of analyses of pollutants and for the evaluation of various analytical techniques. The nongovernmental agencies, such as SCOR and SCOPE, are

hosting workshops and symposia on some of the priority problems in marine pollution.

I suspect that problems will take longer to resolve than in the past. This results from the increased inertia associated with the increased infrastructure in national and international agencies. Still, societal reaction times for stopping unacceptable inputs of materials to the oceans will be short enough for the coastal ocean to cleanse itself of the pollutants.

I will illustrate my optimism using present day activities directed to the problems I have previously considered: toxaphene dissemination, the continuing eutrophication of coastal waters, and the continued usage of DDT and other chlorinated biocides in the developing world.

The SCOPE workshop on the interactions of biogeochemical cycles held in Sweden during May 25–30, 1981 (SCOPE 1983) indicated "Man's activities on earth today include fluxes of carbon, nitrogen, phosphorus and sulfur that are comparable in magnitude to those associated with the natural cycles of these elements. The future likely increases of these during the remainder of the century and the beginning of next can very significantly disturb the global eco-system. . . The most important impacts of these changes (include) the more frequent development of anoxic conditions in fresh and marine water systems and sediments and a trend toward eutrophication of the coastal hydrosphere."

Previously, a NASA workshop (NASA 1980) indicated the limitations of conventional techniques to measure the rate of this cultural eutrophication; these included an inability to make measurements of change in coastal waters available in real time, restricted spatial coverage using ships to investigate changes, and gaps in information between sampling periods. The participants strongly advised NASA to develop remote sensing systems that would provide accurate estimates of the depths of light penetration, the quantity and quality of plant pigments in waters that might be of use in identifying the nature of the algae, and the nature of the nonplant material.

Other groups have expressed similar needs for systematic and continuous surveillances of eutrophication in coastal waters. There are large areas involved, and the changes in the community structures over short time periods may be difficult to detect. Novel approaches to an understanding of the problem are needed to evaluate its seriousness in any given area.

The toxaphene problem is being pursued by at least two top rank laboratories: Ballschmiter and his associates (Zell and Ballschmiter 1980) and Soren Jensen and his associates (Jansson et al. 1979). The former group have initiated a global baseline program for the toxaphene group of compounds inasmuch as they suggest a pollution that could far outrange the known global spreading of compounds of the DDT and PCB groups. The latter workers echo this concern through their finding of toxaphene compounds in Swedish lakes, although the pesticide is not used at all in this nation.

Zell and Ballschmiter (1980) pointed out that the entire ecosphere seems to carry a complex contamination of other organohalogens, as yet unidentified though evident on electron-capture detectors of the gas chromatograph. The awareness that these groups are developing will lead to further elaborations by other laboratories and to actions, if a problem does exist, by regulatory agencies. Thus, undesirable impacts of DDT and HCH in the marine environment will be sought, I predict, with the continuing publication of results about their levels in various geospheres.

The most crucial needs include periodic and continuing meetings in which active scientists can reveal their findings and express their interpretations of them, free of governmental or industrial pressures. Further, international governmental agencies should derive from such meetings appropriate activities that cannot be undertaken by sovereign nations, such as the collection of production and use data of toxic chemicals and quantitative estimates on the disposition of societal wastes to coastal and open-oceans waters. Finally, the use of remote sensing equipment to accommodate the need for global and regional surveys of the impact of pollutants should be continually under assessment.

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Concluding Remarks

A. WALTON

International Laboratory of Marine Radioactivity, International Atomic Energy Agency, Musée Océanographique, Monaco

I wish to begin my remarks with the observation that "Ocean Pollution 1981" has been unique in two ways. First, it was somewhat special in that only single sessions were held, thereby bringing together scientists from several different disciplines at each session and thus enriching the discussion. It was also unique in that scientists from both sides of the Atlantic and elsewhere have been able to come to Halifax, Nova Scotia, giving the conference a truly international flavor.

Further, as we may have noticed, everyone here had their own definition of pollution and I would like to submit a further definition that, over the years, has received a certain amount of international backing and credibility. Marine pollution has been defined by GESAMP (the Group of Experts on the Scientific Aspects of Marine Pollution), as the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairing of the quality for use of seawater and reduction of amenities." Broadly speaking, the conference followed this definition except for the following exceptions: (1) materials having the *potential* to cause harm were also included in the presentations and (2) a number of pollutants, such as "energy" and radioactivity, have been omitted from the discussions. (Editors' note: transuranic radionuclides were deliberately not included for reasons stated in the introduction.)

It was interesting to contrast the discussions that have taken place at this conference with those concerned specifically with other oceanic regions, e.g. the Mediterranean. In the latter region, the countries bordering the sea have already deemed it necessary to have a convention designed to counter the effects of the dangerous trends caused by pollution. With the North Atlantic, no such agreement has yet been contemplated. One may pose the question as to whether this represents a lack of concern on the part of the nations bordering the North Atlantic or whether it arises because the information available to each country suggests that no problem of major significance exists in the region. The results presented here in Halifax should, I believe, be examined in this light by those in positions responsible for decision making.Turning to the scientific program, I offer the following observations on each main theme.

Fossil Fuel Hydrocarbons

It will be recalled that the presentations on this subject ranged from pelagic tar considerations on the scale of the Gulf of Mexico to polynuclear aromatic hydrocarbons at a single station in Chesapeake Bay. We ranged across the Atlantic to the Norwegian sector of the North Sea and in addition were given a lucid presentation of what "comes down the pipe" to Narragansett Bay. Biologically speaking, we heard about some carefully controlled bottle sample degradations and effects studies and finally some pertinent work on clams and fish (even some from the deep sea). The emphasis of all studies was broadly environmental in character, without touching in a major way on ecosystem effects.

What was presented could, from my viewpoint, not be judged to be "shattering," but the papers were nevertheless technically sound. Important points to note, however, were the advances that have been made in analytical approach, chiefly as a result of the wider exploitation of gas chromatography–mass spectrometry. What must be borne in mind, however, is that, even with this highly sophisticated tool, we still remain far removed from being able to make a complete quantitative analysis of a single crude oil. That being the case, how much more difficult is it, analytically speaking, to conduct research in that most

Printed in Canada (J7252)
Imprimé au Canada (J7252)

complex of natural systems, the ocean, with its organic fractions, soluble and particulate, its inorganic constituents at ever-decreasing concentrations, and above all its enormous diversity, biologically and physically. A sense of humbleness must therefore be retained when conducting marine pollution studies and above all a sense of priority in the problems being tackled. It is all too easy to become enamoured of, or indeed to fall in love with, the machine. We are tempted to try and analyze everything just for the sake of analysis. In so doing, we overlook the priorities of the day. We must, therefore, begin to take stock of what constitute the significant problems in organic pollution and use the most appropriate tools and procedures at our disposal in their solution.

Heavy Metals

Spread over 3 days, the conference audience was treated to a delightful pot-pourri of presentations on the metalloids and the heavy metals, which in retrospect gave me, personally, both new information and new insights into oceanic pollution potential. What impressed me most in this group of papers were the following.

1) The fundamental multidisciplinary research studies on Se (not yet finished) and the obvious influence of biological productivity on the occurrence and oxidation states of Se.

2) Speciation studies of metal occurrence are now almost commonplace, largely confirming the occurrence of metals partially bound to organic materials. Oceanic organic matter (being itself a complex mixture) will continue to confound us, however, until our approach becomes more specific in terms of the metals and their various associated ligands.

3) The trend of the 1970's toward detecting lower and even lower concentrations of metals in open-ocean seawater continues, together with the confirmation of contamination and ensuing problems in the earlier sampling and analytical procedures.

4) Heavy metal pollution problems are generally localized in regions of industrial activity. It would appear to me at this time that we do not seem to have an open-ocean problem. Each country has therefore to put its own house in order in this respect.

Ocean Dumping and Site 106

What can be said about this? A participant chairman and four very interesting papers on sewage dumping, acid-iron wastes (1×10^6 t every 3 yr), organic wastes (25–50% being volatile organics), a description of data from a research program on the sources and transport of organics in the general area of the New York Bight, and what appeared to be an argument for deep ocean dumping.

I confess to being left with a not altogether satisfactory feeling after these presentations. While I was not charged with extreme emotion, I was nevertheless left with the feeling that the pressure was on for continued deep ocean dumping of the types described. We were being asked to accept that the recurring presence of eddies at Site 106 makes it a good site for the dumping of waste materials. We were asked to accept a 300-mi-long contaminated zone extending from the dumpsite into the Gulf Stream, and we were being asked to accept a certain measurable damage to the biota of the region. If dumping in the sea is necessary as an alternative to land disposal, then it is my feeling that a new approach is required, perhaps along the lines used by some countries for disposal of radioactive wastes. The idea is not new, but it is worth restating that we should be striving to establish some level of maximum permissible limits that are not to be exceeded.

Finally, with respect to the option of ocean dumping versus land disposal, I believe we are being too narrow in our approach. Our outlook should be broadened so as to include such considerations as where at sea (surface or deep), within or on sediment surfaces, in fjords or other oceanographic features. Such quantitative considerations may have been taken into account prior to the use of Site 106, but the presentation did not support this supposition.

Organic Synthetics

The growing number of new synthetic organic products being introduced on the market demands that an ever-increasing watch be maintained on their environmental behavior and consequences. In this respect, this session was fruitful in that further light was shed on the mechanisms and rates of transfer processes for organic compounds (as a whole) in marine environments. The application of some concepts, however, must remain in question. In particular, the theoretical laboratory work described by Mackay and Shiu appeared, on the surface, to be at odds with the practical observations of Wakeham and his co-workers. It seems that the volatile organics in Narragansett Bay were much more persistent than the theoretical laboratory work would predict.

General

In general terms, it was a little disappointing that no papers were presented that dealt with radioactivity in the marine environment. While I understand the reasons for their not having been included (time limitation), nonetheless the subject is important because the North Atlantic continues to be used as a dumpsite for radioactive wastes, albeit under the supervision of OECD. But this problem can also be turned to our advantage through the quantitative ancilliary information to be gained on various physical and biological marine processes from studies of natural and artificial nuclides. Several laboratories on both sides of the Atlantic are particularly active in this field.

It was also noticeable that chronological studies were conspicuously absent. The importance of such work has been adequately demonstrated in the application of ^{14}C, natural uranium series, and ^{210}Pb dating techniques.

Finally, I was struck by the seeming lack of critical inquiry as to the validity of some of the data that have been presented here. But perhaps that took place in private discussions afterwards. Chemical oceanographic measurements in the past have suffered from inexact data, and without proper intercalibration this problem will persist. The value of such intercalibration experiments was demonstrated markedly in the paper by Holden et al., and it is to be hoped that many more laboratories in the North Atlantic area will be encouraged to participate in future work of this nature.

In conclusion, I wish to return to my first observation that this conference has been unique for its scientific participation on a matter of global importance and significance. Future meetings of this type are necessary and beneficial, not only to the scientific community but also to the public and those in legislative positions. I hope and urge that more meetings such as this one will be held in other regions, dealing with other oceans.

Retrospect and Prospects

JOHN W. FARRINGTON

Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

AND JOHN H. VANDERMEULEN

Bedford Institute of Oceanography, Dartmouth, N.S. B2Y 4A2

The scientific and engineering literature concerned with ocean pollution, including books and reports as well as refereed scientific journal articles, is too voluminous to review in a summary of this type. In addition, it would be presumptuous — indeed, incorrect — to think that all the most important research findings with respect to oceanic pollution in 1981 were presented in the papers or discussed in the conference sessions. However, we are obligated to attempt a broad-ranging summary and conclusion, taking into account the conference papers and the general body of knowledge about ocean pollution. Of necessity, our comments represent our opinions, gathered from discussions with our colleagues and our reading of the literature. They should not be misconstrued as a consensus of the conference participants, because seeking a consensus was not a conference objective.

General conclusions from a broad range of field and laboratory studies around the North Atlantic Ocean led us to express concern about continued pollution of the coastal areas of the North Atlantic. Industrial and urban wastes, dredge spoils, and storm water runoff from cities and towns are sources of chemical pollutants such as fossil fuel compounds, trace metals, and synthetic organic compounds. Valuable living resources of a few coastal areas are contaminated at a level where they pose a risk to human health.

We are able to report that progress has been made in identifying sources of chemical pollution, the rates and routes of movement of those chemicals through marine ecosystems, and chemical and biological processes acting to alter these chemicals once they have entered the oceans. Normal and pollutant concentrations of trace metals in water, sediments, and organisms can be more accurately distinguished. Many more of the known or suspected pollutant synthetic organics can be reliably distinguished than was possible 5 yr ago. It is now possible to distinguish relatively inert from biologically active components of certain pollutants. For example, research of the past 5 yr has demonstrated that initial products of metabolism of petroleum hydrocarbons are more persistent and potentially deleterious than was previously suspected. However, there is a continuing need for stricter attention to interlaboratory analytical methodology and intercomparison and intercalibration exercises, including increased availability of a wide range of standard reference materials. Regional assessments in time and space are severely hampered by restrictions on combining sets of data from different laboratories due to uncertainties apparent in current intercalibration data.

The amounts and varieties of hydrocarbons entering the world's coastal waters are large and contain both toxic and carcinogenic and/or mutagenic components. Many of these become associated with bottom sediments where they may persist for years or decades. While oil spillage no doubt accounts for a considerable amount of the hydrocarbons in the oceans, calculations for urbanized areas of the eastern seaboard of the United States indicate that a far greater amount enters the world's oceans through urban and riverine runoff. Heavily industrialized areas of the North American continental margin have been documented as sources of fossil fuel hydrocarbon contamination that affect their adjacent marine regions.

Metal and synthetic organic contamination are common in coastal waters of the North Atlantic. Trace metal contamination is associated with industrialized and urbanized areas involving large river systems that concentrate the contamination. The contaminant metals originate from a broad range of sources, including various metal-related industries, as well

Printed in Canada (J7361)
Imprimé au Canada (J7361)

as other sources. Not infrequently, the contaminating metal is a by-product of industrial production. Metals may remain in the river water and/or in coastal waters for varying times, but eventually they are deposited in the underlying sediments, often in the heads of estuaries or embayments where they become associated with the finer sediments and represent a toxic threat to fish and shellfish (including scallop and lobster).

Synthetic organics, including a broad range of DDT- and PCB-type compounds and other similar products, are now detected in nearly all environmental samples analyzed. Most of these compounds are toxic to both vertebrate and invertebrate and can be accumulated in seafood. In addition, several are either carcinogenic or mutagenic in minute concentrations. In contrast with petroleum and coal hydrocarbons and with heavy metals, this class of contaminants is a recent man-made phenomenon. These compounds can enter into all levels of the food chain, either from water, prey organisms, or via sediments. In some water bodies entering the North Atlantic and in estuaries, PCBs in fish tissues have risen to alarming levels. This is exemplified by the closing of the commercial fishery in the Hudson River where PCB contamination of such fish species as striped bass (*Morone saxatilis*) has become a health danger.

The progress in identifying chemicals of concern and control of pollutant inputs should not be an excuse for a false sense of complacency regarding chemical pollution of the ocean. In most respects, we are only beginning to understand the complex interactions of natural systems not subjected to significant inputs of chemicals from man's activities. This creates a problem when trying to consider long-term (years) effects of chemical contaminants on specific populations of marine organisms or ecosystems. We have barely crossed the threshold of understanding biological responses of individual species to contaminants.

The research of the late 1960s to mid-1970s indicated that the most immediate concern should be with the more heavily contaminated coastal areas. However, that research also demonstrated that synthetic organic chemicals such as DDT and PCBs had penetrated into the deepest recesses of the North Atlantic abyssal surface sediments and bottom-dwelling organisms only a few decades after first use. Unfortunately, since 1975 very little research on chemical contaminants has been conducted in the open ocean areas away from the nearshore zones.

There were several areas of research that seemed to emerge from the papers and discussions at the conference as worthy of special emphasis.

Estuarine Processes

Although the most extensive knowledge for biogeochemical cycles in this environment is for trace metals, longer term data sets of chemical measurements within the context of carefully designed concurrent physical dynamics are needed for synthetic organic pollutants and fossil fuel compounds. It seems obvious but should be explicitly stated to avoid doubt that chemical pollutant analyses by themselves cannot provide the key answers needed to address the dynamics of these systems. At present, with a few notable exceptions, fluxes of pollutant chemicals to the open ocean through rivers and estuaries are poorly known.

Mesocosms

These experimental tools have proven to be of immense value in understanding biogeochemical cycles, especially in coastal estuarine areas. The most extensive applications have been for studies of fossil fuel compounds, trace metals, and nutrients. Only a few studies focused on synthetic organics have been undertaken. More synthetic organic studies and interactive studies with varying organic loadings (varying degrees of eutrophication) are clearly needed.

Organic Matter

The physical–chemical aspects of biogeochemical cycles such as solid–colloid–particulate matter interactions are strongly influenced by macromolecular organic matter. The organic matter is not well characterized in terms of structural components, and there is only rudimentary knowledge of the nature of the interactions with trace metals, synthetic organic pollutants, and fossil fuel compounds. Yet, it is clear that pathways of movement of pollutant chemicals through marine ecosystems via physical and biological processes depend on the physical–chemical form of these chemicals. This is an area of research in which new concepts and experimental procedures have emerged to tackle a problem that a reading of the literature of the past 20 yr indicates as a persistent, important void in knowledge of biogeochemical cycles.

Monitoring Programs and Intercomparison–Intercalibration Exercises

Despite the constant effort and substantial progress made in analytical chemistry and intercomparison–intercalibration exercises, continued and even accelerated efforts are required. Much-needed monitoring programs to discern if pollution is increasing or decreasing and the rate of change and identification of the more polluted and cleaner areas are often delayed or of little use because of limitations in regional and international data set comparisons due to limited comparability of the various data sets.

This is only one of several problems in regard to monitoring measurements for chemical pollutants. Objectives of monitoring programs are generally not well understood, or worse, even defined. The need for close connections between research and monitoring has often been ignored, and there are unfortunate examples of researchers downplaying much-needed monitoring efforts as second- or third-rate science. Properly designed measurement (monitoring) programs have the potential for substantial contributions to biogeochemical research.

Open Ocean

The measurements of pelagic tar, and to a lesser extent UV–fluorescence-based surveys of dissolved–dispersed petroleum, coupled with a few trace metal profiles constitute the extent of our knowledge of potential or known pollutant chemical distributions in the surface and deep waters of the open North Atlantic Ocean. With very few exceptions (exceedlingly few, given the volume and dynamics of this ocean) our knowledge of synthetic organics is limited to data gathered before 1976.

We think this paucity of data is the result of three factors: (1) the immediate problems of more severe pollution in coastal areas occupied the attentions of qualified researchers, (2) until recently, sampling and measurement problems with trace constituents would have made larger scale expeditions a waste of funds, and (3) the policy of restrictions and controls on dumping of chemicals in the open ocean and restricting coastal discharges as adopted by several nations made a concerted research effort seem to be an unnecessary expenditure of funds.

While coastal pollution problems still must be a high priority, we are concerned with the lack of active research or lack of plans for research on pollutants in the open ocean. The lack of new data and information for open ocean portions of the North Atlanic Ocean raises the question of the status of our knowledge of pollutants in the other oceans.

The Deep Water Dumpsite 106 research described herein is an exception to the above. However, that research is site specific and problem specific. We think that progress in the sampling and analyses for trace chemical pollutants coupled with continued release of these chemicals to the oceans argues for a more general research effort for pollutant biogeochemistry in the open ocean surface and deep waters. Planning should begin

immediately for such efforts and should include a careful consideration of measurements to quantify atmospheric delivery of pollutants to the open ocean as well as mixing between open ocean and nearshore waters. Measurements of synthetic organic compounds in the atmosphere over the oceans have been reported in the literature of the past few years, and calculations based on these few data sets suggest that atmospheric delivery is a major route of transfer of these chemicals to the oceans. Yet, the relative importance of atmospheric inputs and river–estuarine inputs cannot be assessed with present data and knowledge at a level of confidence required for major policy recommendations for reducing pollutant inputs.

Given the large area and volume of the open ocean portion of the North Atlantic and the longtime constants of decades to centuries for processes acting on chemicals once they enter the system, we are very concerned that contemplated, deliberate increases in discharges of pollutant chemicals to the North Atlantic without any increase in our knowledge of oceanic processes via increased research and monitoring will be prejudicial to following generations. We emphasize that the high concentrations of chemical pollutants found in some coastal areas are the result of only 20–30 yr of discharge. Containing and/or reversing these pollution problems has taken or will take many years and will require many millions of dollars.

Waste discharge to the oceans is only one of the many uses man can make of the oceans. Our concern is that this one use be conducted wisely in order that the other desired uses are not unwittingly abrogated.

Papers Presented at the Conference

Guest Address — J. H. STEELE (Woods Hole Oceanographic Institution, Woods Hole, MA, USA)
Change and resilience

Keynote Address — D. C. MALINS (National Marine Fisheries Service, Seattle, WA, USA)
Environmental contaminants and abnormalities in fish and invertebrates from a coast embayment Puget Sound

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Fossil Fuel Hydrocarbons

SESSION CO-CHAIRMEN: J. BUTLER (USA)
D. C. MALINS (USA)

E. S. VAN VLEET, F. F. WEBER JR., AND W. M. SACKETT (USA)
Input of pelagic tar into the North Atlantic from the Gulf Loop current

E. M. LEVY (Canada)
Baseline levels of volatile hydrocarbons and petroleum residues on the Grand Banks

O. GRAHL-NIELSEN, K. WESTRHEIM, AND S. WILHELMSEN (USA)
Chemical monitoring of the marine environment surrounding offshore oil rigs in the North Atlantic

T. L. WADE, R. C. BROWN, AND G. F. OERTEL (USA)
Particulate hydrocarbons and coprostanol concentrations in shelf waters adjacent to Chesapeake Bay

R. BIERI, P. DEFUR, R. J. HUGGETT, W. MACINTYRE, P. SHOU, C. L. SMITH, AND C. SU (USA)
Concentrations of unsubstituted polynuclear aromatic hydrocarbons in a sediment from the Chesapeake Bay

E. J. HOFFMAN, G. L. MILLS, J. S. LATIMER, AND J. G. QUINN (USA)
Annual fluxes of petroleum hydrocarbons to the coastal environment via urban runoff

J. N. GEARING AND P. GEARING (USA)
The effects of suspended load and solubility on sedimentation of petroleum hydrocarbons in controlled estuarine ecosystems

G. J. LEVERSEE, P. F. LANDRUM, T. FANNIN, AND J. P. GIESY (USA)
Effects of humics on polycyclic aromatic hydrocarbons: accumulation by *Daphnia magna* and salting out at estuarine salinities

R. F. LEE AND C. RYAN (USA)
Microbial and photochemical degradation of polycyclic aromatic hydrocarbons in estuarine waters and sediments

J. W. ANDERSON, R. G. RILEY, S. L. KIESSER, B. L. THOMAS, AND G. W. FELLINGHAM (USA)
Natural weathering of oil in sediments: tissue contamination and growth in the clam *Protothaca staminea*

J. E. SOLBAKKEN AND K. H. PALMORK (Norway)
Fate of phenanthrene, a polycyclic aromatic hydrocarbon, in flounder (*Platichthys flesus*)

J. J. STEGEMAN (USA)
Biotransformation of benzo[*a*]pyrene in coastal and deep benthic fish from the western North Atlantic

Session II
Heavy Metals

SESSION CO-CHAIRMEN: H. WINDOM (USA)
J. UTHE (Canada)

A. V. HOLDEN, G. TOPPING, AND J. F. UTHE (UK, Canada)
The use and relevance of analytical intercomparison exercises in monitoring the marine environment

P. G. W. JONES AND D. F. JEFFERIES (UK)
Distribution of selected trace metals in United Kingdom shelf waters and the eastern North Atlantic

P. A. YEATS AND J. M. BEWERS (Canada)
Anthropogenic influences on trace metal distribution in the North Atlantic

A. K. HANSON AND J. G. QUINN (USA)
Distribution of dissolved organically associated copper and nickel in the middle Atlantic Bight

G. T. WALLACE (USA)
Trace element distributions in the Gulf Stream adjacent to the southeastern Atlantic continental shelf — influence of atmospheric and shelf water inputs

D. BEZANSON AND K. KRANCK (Canada)
Adsorption and dispersal of heavy metals in an industrial estuary

D. H. LORING (Canada)
Heavy metal contamination in eastern Canadian coastal and estuarine sediments

D. BUCKLEY AND G. WINTERS (Canada)
Geochemical transport through the Miramichi Estuary

C. D. HUNT AND D. L. SMITH (USA)
Remobilization of metals from polluted marine sediments

W. J. LANGSTON (UK)
Comparative studies on the behavior of arsenic and mercury in U.K. estuaries

J. M. MARKHAM AND K. R. SPERLING (West Germany)
Heavy metals in coastal waters of the German Bight as indicated from seaweeds

J. G. SANDERS (USA)
Role of marine phytoplankton in determining the chemical speciation and biogeochemical cycling of arsenic

J. J. WRENCH (Canada)
Selenium in a coastal ecosystem: natural processes controlling levels, distributions and speciation in surface waters

M. N. HANSEN (Denmark)
Natural variation of element concentrations as indicator organisms

M. A. SHEARS AND G. L. FLETCHER (Canada)
Processes governing Zn^{2+} levels in marine fish

R. WAGEMANN, N. B. SNOW, AND A. LUTZ (Canada)
Heavy metals in tissues and organs of the narwhal (*Monodon monceros*)

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R. RISEBROUGH (USA)

W. C. DE KOCK (The Netherlands)
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D. MACKAY AND W. Y. SHIU (Canada)
Air–sea exchange rates of organic contaminants

B. W. DE LAPPE, R. W. RISEBROUGH, W. R. SISTEK, AND WALKER II (USA)
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J. C. MEANS, T. W. JONES, AND W. R. BOYNTON (USA)
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Persistence of organic pollutants in Narragansett Bay sediments

Conference Overview — A. WALTON (International Atomic Energy Association, Monaco)

Keynote Address — E. D. GOLDBERG (Scripps Institution of Oceanography, La Jolla, CA, USA)
Can we protect the oceans?

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J. W. FARRINGTON, J. M. TEAL, B. W. TRIPP, A. DAVIS, AND J. LIVRAMENTO
Fossil fuel hydrocarbons in sediment and biota of the Northeast U.S. coastal area

F. E. KNOWLES JR.
Chemical differentiation of dredged organic sediments from two southern New England harbors

M. PICARD, D. COSSA, AND J. PIUZE
Teneurs en 3,4,benzopyrene chez *Mytilus edulis* L. de l'estuaire et du Golfe du Saint-Laurent

S. D. MACKNIGHT AND M. S. HUTCHESON
Heavy metals in the sediments of the Restigouche River

R. W. TRAXLER, E. M. WOOD, AND S. C. LONEGRAN
Heavy metal pollutants: distribution and microbial interactions in Narragansett Bay

A. S. W. DEFREITAS AND B. K. FRUEDEL
Methylmercury accumulation from water by *Daphnia magna* (Strauss)

A. FODA, J. WRENCH, AND J. H. VANDERMEULEN
Conversion and cycling of a heavy metal (selenium) by marine bacteria

S. BRADDON
Relationship of selenium to mercury and biochemical interaction with fish macromolecules

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Canadian Journal of Fisheries and Aquatic Sciences (Supplement)

Journal canadien des sciences halieutiques et aquatiques (Supplément)

CJFSDX40(SUPPL. 2) 1–362 (1983)
ISSN 0714-7937

Volume 40, Supplement No. 2, 1983 Volume 40, Supplément n° 2, 1983

Correct citation for this publication:
FARRINGTON, J. W., J. H. VANDERMEULEN, AND D. G. COOK [ed.] 1983. Proceedings of the Conference on Pollution in the North Atlantic Ocean. Can. J. Fish. Aquat. Sci. 40(Suppl. 2): 1–362.

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